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Applications of the olefin metathesis reaction; Application of carbon-hydrogen bond activation to the surface oxidation of polypropylene and polyethylene

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I. APPLICATIONS OF THE OLEFIN METATHESIS REACTION

II. APPLICATION OF CARBON-HYDROGEN BOND ACTIVATION TO THE SURFACE OXIDATION OF POLYPROPYLENE AND POLYETHYLENE

A Dissertation Presented

by

CATHERINE G. COLEMAN

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To my Mom,

who brought me up to believe

I could be anything I wanted to be...

ACKNOWLEDGMENTS

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This page is not nearly large enough to list the many people who have helped me during my graduate career. Sometimes just a little help at the right time made a big difference and I hope that those people know who they are. A final thank you goes to my incredible family; their love and support has meant the world to me.

ABSTRACT

PART I. APPLICATIONS OF THE OLEFIN METATHESIS REACTION

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Applications of the olefin metathesis reaction to the areas of conducting polymers and crosslinked systems were investigated. Metathesis of *cis*-3,4-dichlorocyclobutene and 3-acetoxycyclobutene was studied with the $WCl_6/SnMe_4$ and $Re_2O_7/SnMe_4$ catalyst systems to produce processable precursors to polyacetylene. Polymerization of *cis*-3,4-dichlorocyclobutene with both catalsyts yielded a black particulate solid which was characterized as a partially chlorinated form of polyacetylene. Metathesis of 3-acetoxycyclobutene with $WCl_6/SnMe_4$ resulted in the formation of a complex between the metal and the acetate functionality. Metathesis of 1,3-cyclooctadiene to produce an alternating copolymer of acetylene and cyclohexene resulted in negligible amounts of free cyclohexene when run above ceiling temperature conditions for cyclohexene, indicating that 1,3-cyclooctadiene had polymerized predominately via a non-metathesis mechanism.

syn-Tricyclo[4.2.0.$0^{2,5}$]octa-3,7-diene (TCOD) was synthesized for use as a metathesis crosslinking agent. Solution studies with the $WCl_6/SnMe_4$ catalyst system showed that TCOD could be homopolyerized and also copolymerized with cyclooctene. NMR analysis of the copolymers indicated cyclobutane crosslink junctions. Copolymer-

ization of TCOD with cyclooctene and norbornene using $WCl_6/EtAlCl_2$ gave solid samples which were characterized by swelling and shear modulus measurements. When compared with samples containing TCOD, the control samples (no TCOD) demonstrated a distinct increase in the degree of swelling and a drop in modulus at higher temperatures.

Carbon-hydrogen bond activation chemistry was applied to reactions at polymer surfaces to selectively place hydroxyl groups on hydrocarbon polymer surfaces. Four reagents were studied: stannous chloride/oxygen, *meta*-chloroperbenzoic acid, methanol/benzoylperoxide and trifluoroperacetic acid(TFPAA). Reacted surfaces were analyzed using XPS, ATR-IR, UV, contact angle and gravimetric analysis. The decrease in both the advancing and receding contact angles for the products of each of these reactions indicated an increase in surface energy, and XPS results showed that oxygen had been incorporated onto the surfaces. Kinetics of the TFPAA reaction were studied over a 24 hour period. The reaction proceeded deeply and rapidly (>1 μm/15 min) to produce a modified surface of hydroxyl and trifluoracetate groups as well as some ketones and non-halogentated ester groups. Base catalyzed hydrolysis, reduction with borane/THF and labeling studies with heptafluorobutyrlchloride showed that the surface-bound functional groups which result from the TFPAA oxidation of polypropylene and polyethylene can act as useful reactive handles for further modification.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SCHEMES

PART I. APPLICATIONS OF THE OLEFIN METATHESIS REACTION

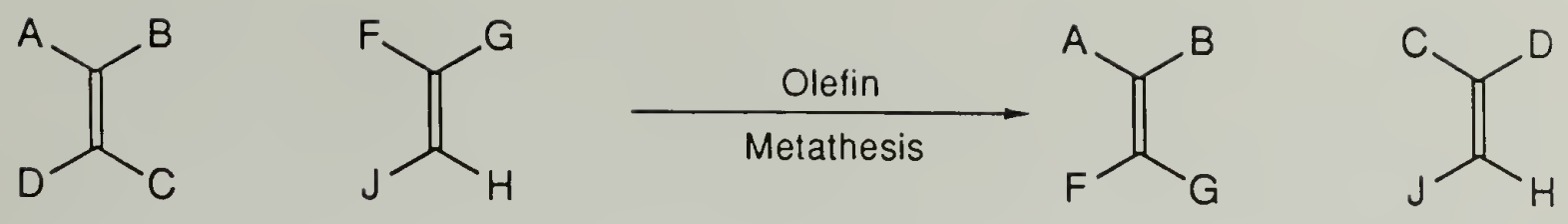
CHAPTER 1

INTRODUCTION

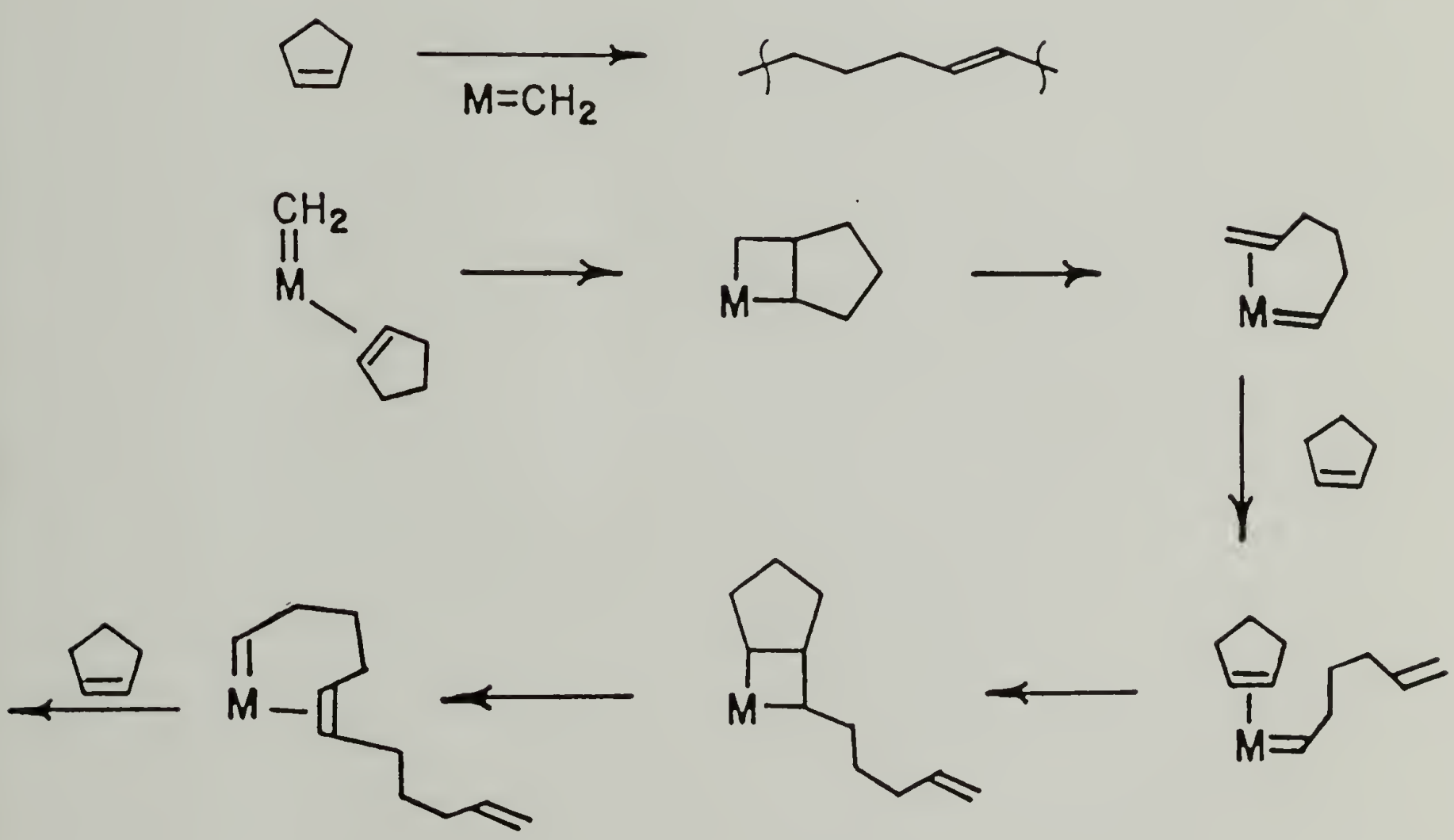
Overview

The olefin metathesis reaction has fascinated a broad spectrum of researchers and its development has crossed the boundaries of organic, inorganic, organometallic, catalytic, theoretical and polymer chemistry. Metathesis catalysts have been used to produce specialty chemicals, commercial rubbers, engineering plastics, and more recently, graft and block copolymers. Ring opening metathesis polymerization (ROMP) of functionalized cyclic alkenes gives polymers with unsaturation in the main chain, as well as reactive "handles" for further derivatization; a range of new materials is possible with appropriately substituted monomers. Careful manipulation of reaction conditions with select catalyst systems allows for precise control of chain microstructure. The unique products available from this reaction and its fast paced development have insured its place in history for exciting applications which have yet to be invented.

A general reaction scheme is shown in Scheme 1.1 to illustrate the products of acyclic and cyclic olefin metathesis. In the acyclic case, the products are olefins which appear to have "changed partners" or substituents. For cyclic olefins, the products are polymers which retain the repeat unit of the cyclic olefin and incorporate its double bond into the main chain. Several recent reviews of both cyclic and acyclic metathesis are available.[1-3] In the research presented in this dissertation, we capitalized on some of the unique aspects of olefin metathesis polymerization and explored a few of the many applications of this fascinating reaction to the field of material science. Specifically, we targeted the areas of conducting polymers and crosslinked systems.



Metathesis of Acyclic Olefins



Metathesis of Cyclic Olefins

Metallo-Carbene Mechanism (M=W, Re, Mo, etc.)

Scheme 1.1. Metathesis of Cyclic and Acyclic Olefins

In the case of conducting polymers, we took advantage of the fact that metathesis of cyclic olefins produces polymers with double bonds in the main chain. If the monomers were selected such that the resulting polymers could be easily converted to conjugated systems, the products would resemble polyacetylene, a known organic conducting polymer. Because the initial metathesis products would not be fully conjugated, they should not be as intractable as polyacetylene. In short, we wanted to employ metathesis catalysts to synthesize processable precursors of polyacetylene. Before their transformation to polyacetylene each of these initial metathesis polymers could be described as a "Latent Conducting Polymer."

Our second investigation addressed the need for a well behaved crosslinking agent for metathesis polymerizations. To date, several crosslinked polymers have been reported as a result of metathesis polymerization through another double or triple bond in the monomer, or as a result of more than one operative polymerization mechanism.[4] In the second part of the metathesis portion of this dissertation, *syn*-tricyclo [4.2.0.$0^{2,5}$]octa-3,7-diene (TCOD) was synthesized as a metathesis crosslinking agent. Both double bonds in the tricyclic system should be extremely reactive in metathesis polymerizations because of the considerable strain in the cyclobutene rings. As a result, incorporation into the network should be quantitative and the crosslink density should be proportional to the ratio of TCOD to monomer. Being able to define the distance between crosslinks in a network as a result of using a crosslinking agent with a consistent degree of functionality is critical to our ability to tailor the physical properties of a network.

History

Historically, commercial industry has been a prominent supporter of the development of the olefin metathesis reaction, as reviewed by Streck[5,6] and Banks.[7] As early as 1954, norbornene (NBE) was polymerized at Dupont with a homogeneous

titanium-based catalyst to form an unsaturated hydrocarbon polymer.[8] In the same laboratory, Eleuterio polymerized cyclopentene and other cyclic olefins in 1957 over a heterogeneous molybdena-alumina catalyst.[9] At about the same time, Robert L. Banks at Phillips Petroleum and a team of researchers led by Natta at Montedison found that in the copolymerization of ethylene and acyclic and cyclic olefins, two distinct types of polymers were produced through an "olefin disproportionation" process. One retained the ring structure of the monomer and the other retained the double bond character of the same monomer.[10-12] The latter type were referred to as polyalkenamers or polyalkenylenes by Natta's co-worker Dall'Asta.[13] Calderon et. al. at Goodyear Tire and Rubber Co. established that the polymerization of cyclooctene (COE) and 1,5-Cyclooctadiene (COD) gave a series of macrocyclic oligomers and they coined the phrase "metathesis" in their report of the homogeneous disproportionation of pentene.[14] Their extensive study spurred a number of different research groups to investigate what quickly became the most intriguing reaction of the decade.[15]

A general mechanism for metathesis, centering on a "quasi-cyclobutane" complex, was first proposed by Bradshaw.[16] In this mechanism, alkylidene fragments were exchanged "pairwise" between two olefins and arguments focused on whether the cyclobutane complex represented a transition state or an intermediate. Chauvin was the first to propose the metal-carbene mechanism which is generally accepted today.[17] Definitive support for his theory came from a series of double cross-metathesis experiments by Katz and McGinnis.[18] General routes to carbenes were developed[19-20] and then Tebbe and Schrock demonstrated metathesis systems which used recoverable metal carbenes. Experiments by Grubbs[21] showed the interconversion of a carbene-olefin and a metallocyclobutane leading to the generally accepted mechanism of propagation by 2+2 addition of an olefin to a metal carbene complex to give a metallocyclobutane intermediate, as shown in Scheme 1.1. Ring-opening rearrangement generates a new

metal-carbene complex and a new olefin. In the case of cyclic olefins, the second olefin becomes part of the unsaturated polymer, growing from the metal center.

The metathesis reaction was first applied industrially to produce high quality ethylene and 2-butene from propene in a process still known today as the Phillips Triolefin Process. Other industrial applications include the metathesis of terminal olefins to form a mixture of products which is then fractionated. The C_6-C_8 range can be further reacted and used to make alcohols for use as plasticizers and the C_{12}-C_{15} range can be arylalkylated and sulphonated to make detergents.[22-23] A variety of specialty chemicals can be produced by metathesis of functional group-containing molecules to form a variety of sex and insect pheremones[23-25] and the precursors to active ingredients in perfumes. Heterogeneous metathesis catalysts are especially useful because the catalysts can be regenerated and product separation is facile. In addition to specialty chemicals, several polymers are produced on commercial scale with metathesis catalysts. The commercial appeal of trans-polypentenamer was responsible for much of the early interest in ring-opening polymerization of cyclic olefins in the early seventies. Other commercially produced metathesis products include poly(norbornene) which is known commercially as Norsorex™, poly(octenamer) which is a soft rubber called Vestenamer™[265] and poly(dicyclopentadiene) which is a tough impact-resistant plastic marketed under the name Metton™ by Hercules.[5,27]

Catalyst Systems

Catalysts for olefin metathesis are generally derived from transition metals in groups IVa-VIII, the most active ones being Mo, W, and Re.[2] The active species is a metal carbene which is usually formed with the assistance of a cocatalyst from the main group metal alkyls. A group of commonly used cocatalysts includes BuLi, $EtAlCl_2$, R_3Al and R_4Sn. For many traditional metathesis catalysts, the active species is thought to be

formed by the abstraction of a hydrogen from an alkyl ligand on the cocatalyst. Subsequent reductive elimination results in the formation of a metal carbene coordinates substrate olefins to produce metathesis products, as shown in Scheme 1.1. Catalyst activity can depend strongly on the order of mixing, aging time, solvent and temperature. The homogeneous systems can be active at room temperature, while the heterogeneous ones operate at higher temperatures, in excess of 450°K. Supported systems based on Re are the exceptions, showing high activities even at room temperature. These transition metal carbene complexes also catalyze olefin isomerization and dimerization, depending on the coordination number and the stability of the metal-carbene complex.[28,29]

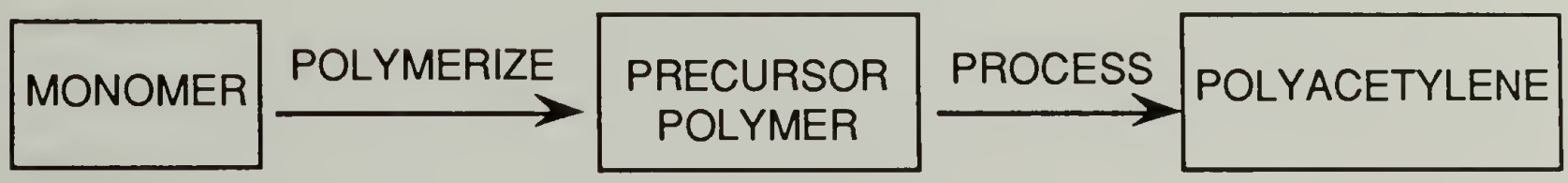
Applications of Metathesis to Conducting Polymers

The field of organic metals has seen a deluge of activity in recent years.[30-32] These materials are typically polyconjugated systems which can be doped via the addition of an electron donor or acceptor to become semi-conducting or even metallic-type conductors. These novel organic conductors exhibit excellent electronic properties, but the same conjugated double bonds which lend themselves to metallic conductivity after doping present a considerable obstacle to processing and fabrication. Films prepared by the Shirakawa method have little or no mechanical integrity and cannot be formed into different shapes after polymerization. Consequently, they cannot be easily incorporated into electronic devices.[33,31]

We are not the first to set our sights on synthesizing polyacetylene or other polyconjugated systems using metathesis catalysts. Korshak has reported the polymerization of cyclooctatetraene[34] to form an intractable black solid in low yields, and several groups have taken advantage of the precursor route made popular by Feast and Edwards,[35] which will be discussed in more detail in a later section. Recently, Robert Grubbs has applied some of the newer alkylidene catalysts toward conducting polymer

synthesis.[36-38] His success in polymerizing alkyl-substituted cyclooctatetraenes has led to soluble materials whose conductivity and processability can be controlled via copolymerization with other cyclic olefins.

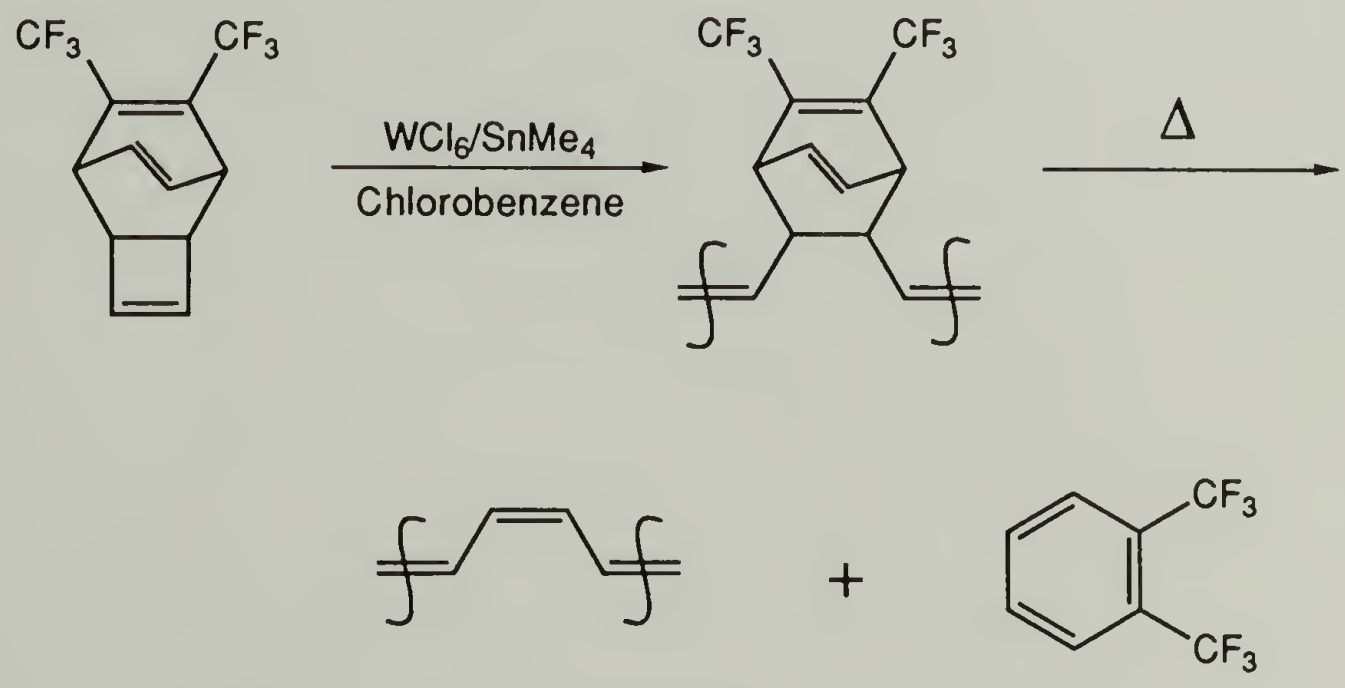
Our goal in the work described in this dissertation was to use the olefin metathesis reaction to further expand the synthetic routes available for the production of polyacetylene. Our plan was two-fold. In our first approach, we addressed the issue of processability: Metathesis polymerization of substituted cyclic olefins should produce stable, processable polymers which already have double bonds incorporated into the main chain. A judicious selection of monomers should give a polymer which can be converted in a controlled manner in polyacetylene. The initial polymer products are precursors to polyacetylene and can be thought of as latent conducting polymers. They should be amenable to processing and fabrication. A generic scheme illustrating the precursor approach is shown in Scheme 1.2.



Scheme 1.2. The Precursor Approach to Polyacetylene Synthesis.

Our second approach to latent conducting polymers also takes advantage of the double bonds contained in the product polymers, but in this case we exploited the unique ability of these catalysts to form cyclic oligomers via backbiting reactions. Polymerization of 1,3-COD should yield a polymer which is a copolymer of cyclohexene and polyacetylene. Cyclohexene should not be reincorporated into the polymer under the reaction conditions, and eventually backbiting reactions by the active catalyst species should produce polyacetylene and free cyclohexene.

Both of these pathways should lead to polyacetylene via LCP or precursor polymers which are expected to be soluble and tractable before their transformation into electrically conducting materials. As mentioned previously, the precursor approach to polyacetylene is not unique. This route was pioneered by Edwards and Feast[32,35,39-43] and has been explored extensively by several other groups as well.[44,45] The Feast route is summarized in the Scheme 1.3.[35] Metathesis of these tricyclic ring systems gives

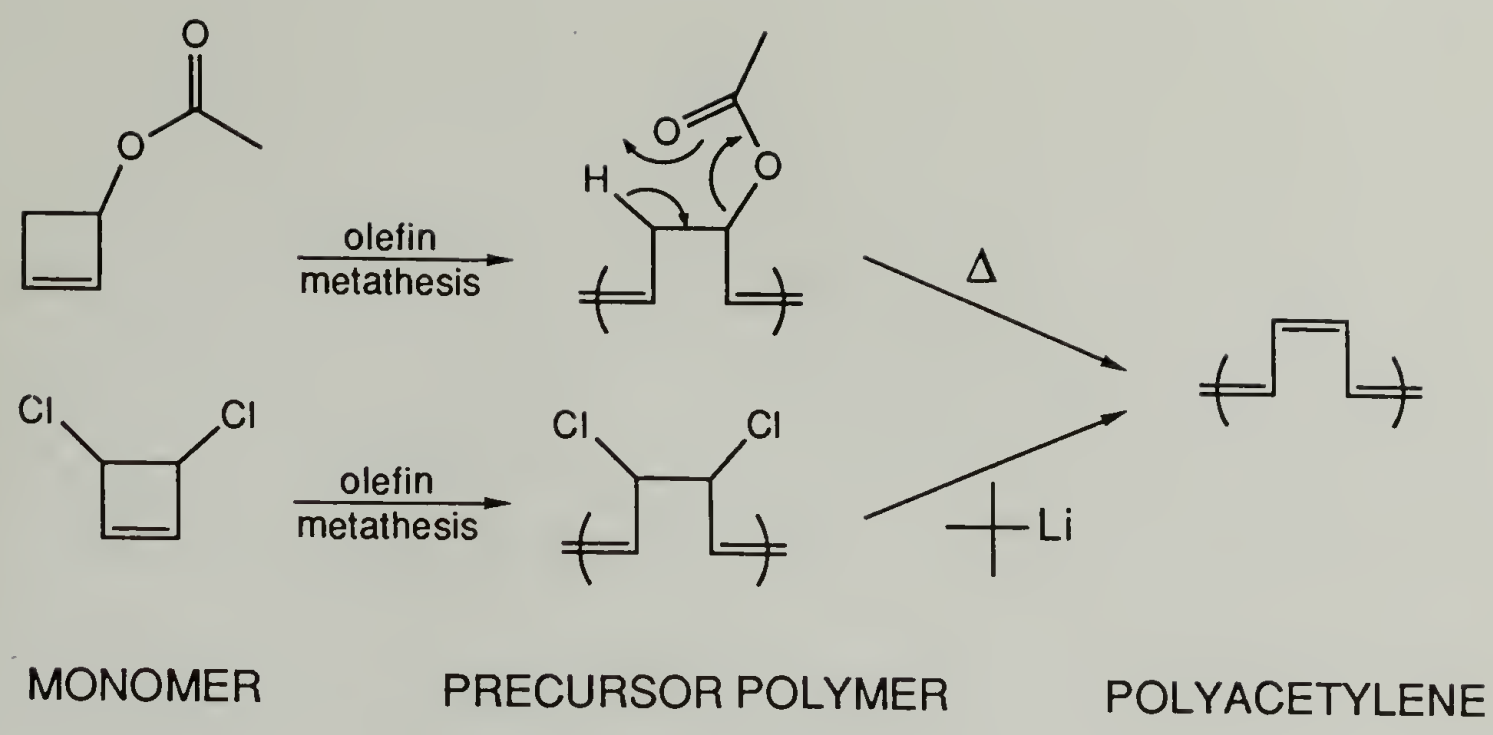


Scheme 1.3. The Durham Route to Polyacetylene Synthesis.[35]

precursor polymers which can be either pyrolyzed or reacted electrochemically to produce what has become known in the literature as Durham polyacetylene, in reference to the geographic location of the earlier developments. Others have further developed the processing of these materials to form oriented fibers and films which display anisotropic physical properties.[46-49] To their credit, those who have pursued the Feast approach have been successful in the metathesis polymerization these of types of molecules, despite the presence of potentially incompatible functional groups within the ring systems. In all of these examples however, either the monomers were expensive or complicated to synthesize, or the by-products produced in the transformation to polyacetylene have been difficult to remove cleanly. Intermediate products, other than polyacetylene, were produced during the transformation processes, leading to chemically inhomogeneous materials. Trapped impurities can disrupt the order in the sample and can add considerably to the uncertainty in the conductivity measurements of doped samples. Ideally, we would like the eliminations to be facile; more volatile by-products and cleaner transformations would produce more chemically and physically homogeneous materials.

Metathesis Polymerization of Substituted Cyclobutenes

Our approach to the synthesis of processable precursors of polyacetylene using cyclobutenes is detailed in Scheme 1.4. Conveniently, the metathesis polymerization of 3,4-substituted cyclobutenes should yield alternating copolymers of acetylene and substituted ethylenes. The ethylene character of these polymers should enhance solubility properties so that they can be processed into appropriate shapes and then converted in-situ into PA. We specifically chose these substituted cyclobutenes because their polymeric



Scheme 1.4. Synthesis of Polyacetylene via Metathesis Polymerization of Substituted Cyclobutenes.

metathesis products were only a single elimination reaction away from polyacetylene. Metathesis, followed by elimination should render mixtures of *cis*- and *trans*- PA. The initial metathesis polymers should be soluble in common solvents and stable enough to be processed under mild conditions.

Cyclobutenes were first polymerized with metathesis catalysts by Dall'Asta and Natta[50] and the products obtained by them and other researchers were reviewed by Ivin.[51] More than one type of product is possible; catalysts based on Ti, V, Mo, W and Re typically produce ring-opened products, while catalysts based on V, Cr, Rh and Ni produce addition products which have polymerized across the double bond and still retain the closed four-membered ring in the polymer. Based on reports that 1-trimethylsilyl cyclobutene[52] and 1-methyl cyclobutene[53] polymerize with a head-tail (HT) bias, we hoped that the acetoxy derivative would also polymerize in a stereoregular manner.

3,4-Dichlorocyclobutene We chose 3,4-Dichlorocyclobutene (DCCB) as the first candidate monomer in these studies because it was synthetically accessible[54-56] as well as commercially available, and because the transformation to PA from the parent metathesis polymer could be achieved by a variety of literature methods.[57] In addition, a number of interesting metathesis candidates could be synthesized from the DCCB monomer if this work proved successful.

Brunthaler and Steltzer metathesized DCCB[58] for many of the same reasons that we did. They concluded that poly(DCCB) reacted in the presence of the catalyst to form a chlorinated polyacetylene moiety. At the time that their work was published, we had synthesized DCCB and were ready to begin polymerization studies. We chose to repeat Brunthaler's work for reproducibility and to continue with our own studies, using different polymerization conditions. We wanted to examine the metathesis homopolymerization of DCCB as well as its copolymerization with norbornene, using both homogeneous ($WCl_6/SnMe_4$) and heterogeneous ($Re_2O_7/SnMe_4/Al_2O_3$) metathesis catalyst systems.

3-Acetoxycyclobutene. We selected 3-acetoxycyclobutene (ACB) as the second cyclobutene monomer because the synthesis had been reported[59-61] and the metathesis polybutenamer product can be reacted via a *syn*-pyrolytic elimination to form polyacetylene. This type of elimination has been reported for many different types of acetoxy derivatives[57,62] and has several attractive features. First, the elimination conditions are mild enough (~100°C) that we do not expect degradation of the parent polymer or of the polyacetylene product derivative. Second, the elimination should not be catalyzed under metathesis polymerization conditions if reasonable temperatures are employed. As a result, the transformation to polyacetylene can be carried out in a controlled manner and acetic acid should be the sole by-product.

Functional Group Compatibility

Catalyst systems were carefully chosen for the polymerization of DCCB and ACB. Hundreds of olefin metathesis catalysts have been reported, each with advantages and disadvantages, depending on the type of metathesis and the olefins in question. Functional group metathesis is one of the most exciting aspects of the reaction being developed today, due to the types of specialty chemicals that it makes available, but it is also one of the more challenging. In many instances, the same functional groups which provide interesting properties to the end products are poisonous or at least inhibitive to most metathesis catalysts. In fact, the first report of the metathesis of a functionally substituted acyclic olefin occurred as late as 1972 when Van Dam[63] et. al. reported the metathesis of unsaturated esters with the homogeneous $WCl_6/SnMe_4$ system. Since then, the list of metathesis compatible functional groups has grown to include several oxygen containing groups such as esters[63-70] and ethers,[71] plus amines,[72] halogens[41-43,73-75] and some sulphur compounds.[76] Applications to pheremone and fragrance synthesis as well as to other specialty chemicals have driven developments in the area of functional group metathesis.[63,70-77] For example, methyl-9-decenoate, a key precursor to the Queen Bee Substance (honey bee pheremone) can be made from the metathesis of methlyoleate and ethylene.[78] Several reviews of functional group metathesis are available.[2469,79-80]

Streck[26] reviewed the metathesis behavior of tungsten-based metathesis catalysts toward 150 different unsaturated compounds, many of which contained functional groups. The metathesis activity of these transition metal catalysts with functional group-containing compounds can be several orders of magnitude lower than with ordinary olefins, because the strong interactions between the polar groups and the metal hinders coordination. He classified their presence in the reaction mixture as inhibitive, inert, activating or actively participant, and he rationalized effects by the change in electron density at the central

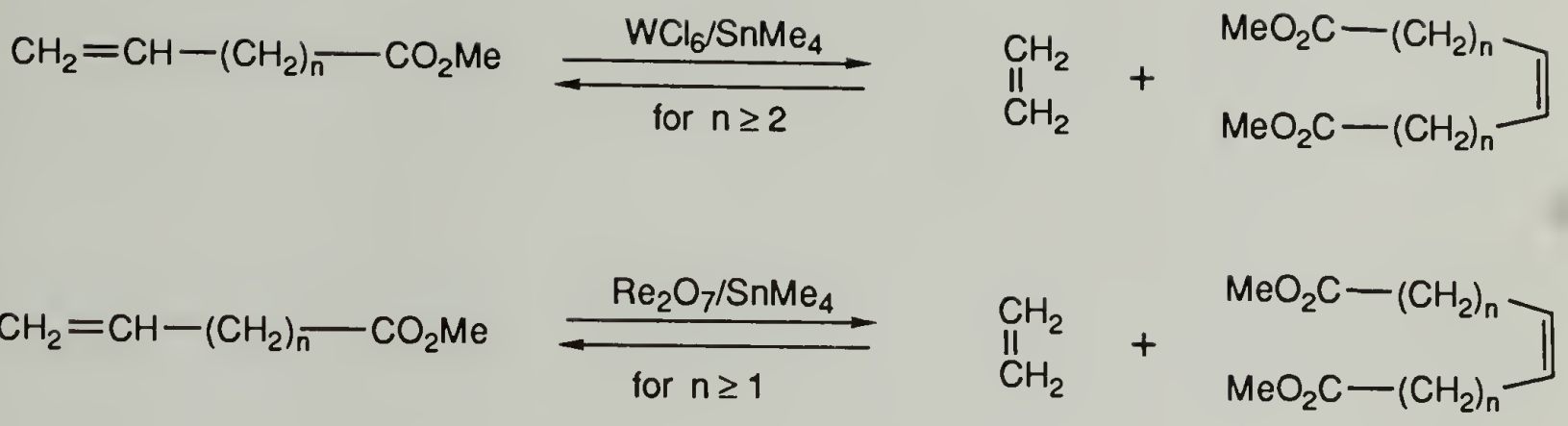
tungsten atom. Grubbs summarized the interference effects of functional groups on olefin metathesis by the following:[81]

1) The functional group reacts with the cocatalyst, preventing it from reacting with the metal to form the active species.
2) Reactions between the metal and the functional group destroy the active centers.
3) Competitive complexation between the functional group and the olefin retards constructive metathesis.

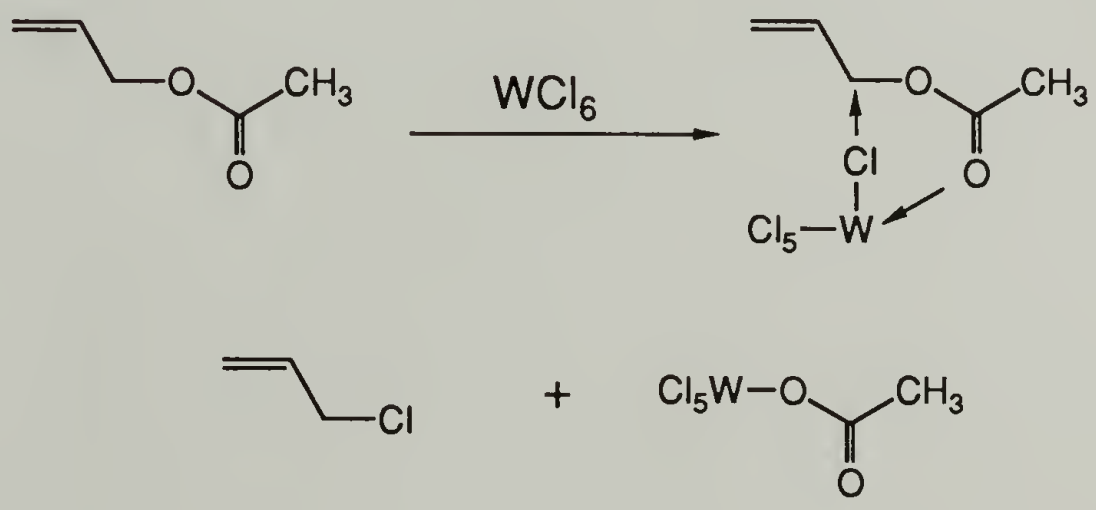
In the case of oxygen containing functionalities, Grubbs suggested that the driving force behind inhibition was the formation of an oxo-metal bond.

As a traditional rule of thumb, functional groups had to be separated from the metathesizable double bond by at least two methylene units. As shown below in Scheme 1.5,[69] it was commonly believed that productive metathesis occurred only for systems where $n \geq 2$.[6971,82] At the time that this project was conceived, the only exception to this rule was work published by Mol and Woerlee[83] reporting the metathesis of allyl acetate, allyl ethyl ether and allyl bromide (n=1) using $Re_2O_7/SnMe_4$ on alumina. With the homogeneous $WCl_6/SnMe_4$ system, Verkuijlen obtained only allyl chloride from allyl acetate;[69] he suggested the reaction pathway shown in Scheme 1.6. Mol's work showed that for the heterogeneous $Re_2O_7/SnMe_4/Al_2O_3$ system, $n \geq 1$ applied, in contrast to the $n \geq 2$ rule that applies to homogeneous systems.

Despite the close proximity of the functional groups to the double bond, we were optimistic about the metathesis polymerization of substituted cyclobutenes even with homogeneous catalysts. Several groups have shown that the reactivity of strained rings systems toward metathesis catalysts can compensate for the steric and electronic factors that reduce the reactivity of these types of monomers.[84] The structure of the strained ring



Scheme 1.5. The n ≥ 2 Convention: Metathesis of Functionalized Olefins with the $WCl_6/SnMe_4$ and $Re_2O_7/SnMe_4/Al_2O_3$ Catalyst Systems.



Scheme 1.6. Metathesis of Allyl Acetate with the $WCl_6/SnMe_4$ Catalyst System.

can prevent undesirable reactions between the functional group and the metal because the functional groups may not be able to get close enough to interfere with metathesis when the cyclobutene rings coordinate to the metal. If metathesis occurred quickly enough to compete with complexation of the functional group at the active center, then metathesis products should be formed.

McCarthy and Patton established that the structure of the propagating carbene determines the rate of metathesis polymerization.[85] The carbenes formed in the metathesis polymerization of DCCB and ACB should be more reactive than ordinary cyclobutene carbenes because the functional groups adjacent to the nearest double bonds make those bonds unattractive for complexation. Without the penultimate double bond coordinated, new monomers can approach more easily and the carbene is more reactive. Subsequent metathesis reactions between the polymer chain and the catalyst are unlikely for the same reasons; the double bonds on the polymers can be more hindered than those on the monomers due to the functional groups present. For DCCB, the bulky chlorine groups should prevent any backbiting reactions once the rings have opened[38,58,86] and only linear polymers, as opposed to cyclic oligomers, should be formed.

Catalyst Systems for Latent Conducting Polymer Synthesis

We chose the $WCl_6/SnMe_4$ and $Re_2O_7/SnMe_4/Al_2O_3$ catalyst systems because they were widely accepted as the most functional group-tolerant of the homogeneous and heterogeneous metathesis catalysts, respectively. Both are commonly available, easy to prepare and compatible with the functional groups proposed.[69,77,79] Systems based on ruthenium and osmium[43,87] are also compatible with functional groups, but the tungsten and rhenium systems are more versatile and have more firmly established precedents in the literature.

$\underline{WCl_6/SnMe_4}$. We chose the $WCl_6/SnMe_4$ system as our homogeneous catalyst because of its long history of functional group compatibility and its reputation for high selectivity and activity.[24,69,77,88] The metathesis of a variety of compounds has been reported with this system, including, but not limited to esters[63-66,68,70] ethers,[71] chlorinated[73-75] and fluorinated olefins,[42-43] amines,[72] and several sets of prepolymers or oligomers with functionalized endgroups.[66,72,77,89] The volume of $WCl_6/SnMe_4$ work on the metathesis of esters was especially encouraging for our plans to polymerize ACB. We were also encouraged by Feast's report of $WCl_6/SnMe_4$ compatibility with chlorinated polycyclic unsaturated compounds.[32,74]

Other cocatalysts, including other tetraalkyl/aryl tin derivatives and alkyl aluminium compounds are frequently used with WCl_6,[2] but $SnMe_4$ is the most common when functional groups are present.[47,69] Ratios of tungsten to tin are reported from 1:1 to 1:7, with 1:2 being one of the most often cited.[90] Metathesis reactions with functional group considerations necessitate higher concentrations of catalyst with respect to monomer. Ratios of WCl_6:Monomer of 1:10 to 1:200 are not uncommon.[32,63,70,91] The need for higher than normal concentrations of catalyst in these reactions was demonstrated by Ast[71] in his studies of the self- and co-metathesis of unsaturated esters. Ratios of $WCl_6/SnMe_4$/Ester of 1:3:100 resulted in negligible self-metathesis and only slightly better results for cometathesis. An increase in catalyst concentration to 1:3:30 gave small increases, and reactions run at 1:3:10 were clearly more efficient for both processes. Polymerization of functional group-containing olefins also dictated higher temperatures in order to overcome the increased barriers to coordination for these compounds. Typically, reaction temperatures ranged from room temperature to 110°C[63,69-70] for these types of polymerizations. Reaction times on the scale of days were not uncommon for polymerizations involving functionalized monomers.[70]

$\underline{Re_2O_7/SnMe_4/Al_2O_3}$. We chose the $Re_2O_7/SnMe_4/Al_2O_3$ catalyst system as a second way to metathesize DCCB and ACB for several reasons. First, it was a heterogeneous as opposed to a homogeneous system. Second, similar to its tungsten-based counterpart, it also had a strong reputation for functional group compatibility under mild reaction conditions.[69,77,79,92-94] Historically, it was the first heterogeneous catalyst system to demonstrate metathesis of unsaturated esters with methyl 4-pentenoate.[95] Mol's report of the acyclic metathesis of vinyl acetate using this catalyst was promising for our work with ACB.[83]

Similar to most of the transition metal compounds capable of metathesis, this system also requires the aid of a cocatalyst. Re_2O_7/Al_2O_3 alone does not metathesize compounds with polar functionalities, but the addition of even small amounts of $SnMe_4$ raises catalyst activity by several orders of magnitude.[96] Boelhouwer claims that the reduction of Re is a necessary condition for metathesis activity,[97] and Mol asserts that the tin stabilizes the O^{2-} species which in turn stabilizes the active sites.[98] The alkyl tin reduces the activated Re-Al species to a more favorable oxidation state for olefin metathesis.

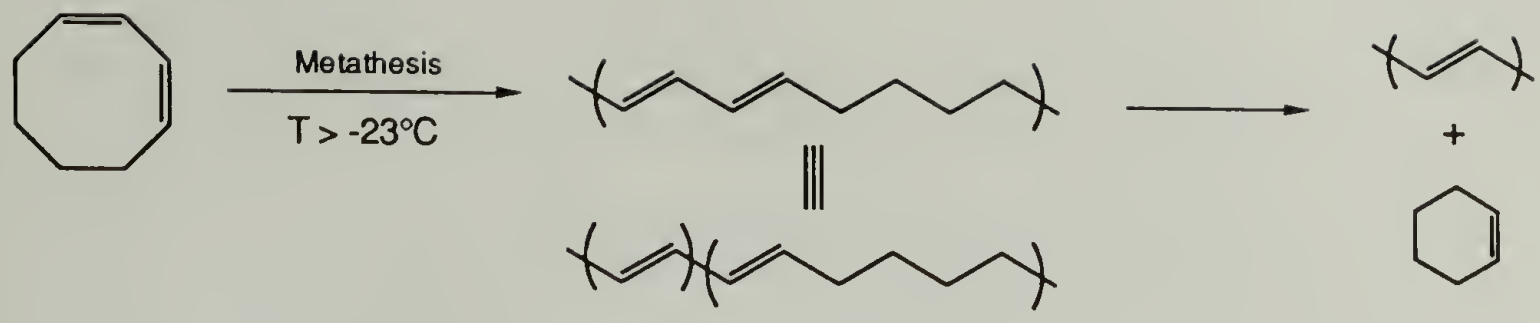
The oxidation state of rhenium oxide and correspondingly its metathesis activity depends on temperature, moisture, water content and catalyst loading with respect to the support. $Re_2O_7/SnMe_4/Al_2O_3$ is prepared by impregnating γ-Al_2O_3 with an aqueous solution of ammonium perrhenate followed by calcination at 550°C.[99] During calcination, the NH_4ReO_4 decomposes to form what is formally referred to as Re_2O_7. Like many of the traditional metathesis catalysts, the oxidation state and exact chemical composition of the active species have not been determined, but the steep increase in metathesis activity with increased rhenium content is clear.[100-103] At low catalyst loadings, the surface is made up of mostly monomeric rhenium ions which are stabilized by Al-O-Re bonds. At

increased loadings (>13%), the Re-O-Re dimer structure becomes more important. An elegant set of temperature programmed reduction experiments with various heating rates showed an increase in activation entropy with increasing Re content.[104] These suggested that at low concentrations, poor reactivities were the result of steric hindrance; the catalyst was buried in the valleys of the Al_2O_3 surface,[101] hindering rotation of the activated complexes. We used 15% Re_2O_7/Al_2O_3 in these studies, which is considered a high loading of catalyst. Similar to the situation with $WCl_6/SnMe_4$ for the metathesis of functionalized olefins, increased concentrations of catalyst (<200/1 olefin to Re)[95] and higher than normal reaction temperatures (30-100°C)[69] are also reported for the $Re_2O_7/SnMe_4/Al_2O_3$ system.

Metathesis Polymerization of 1,3-Cyclooctadiene

Our second approach to synthesizing PA takes advantage of the ability of metathesis catalysts to backbite and react with the polymer chains that they have produced by ROMP of cyclic olefins. In the cyclobutene polymerizations, we used the non-backbiting tendency of the catalyst with functionalized monomers to our advantage in order to form well defined polymer chains instead of a series of cyclic oligomers. In the polymerization of 1,3-cyclooctadiene (1,3-COD), we took the opposite tact.

Metathesis of 1,3-COD produces poly(1,3-COD), which is an alternating copolymer of acetylene and cyclohexene. As shown in Scheme 1.7, further interaction of the metathesis catalyst with the polymer to form cyclic oligomers should ultimately yield CXE and polyacetylene, if the reaction is run outside of ceiling temperature conditions for cyclohexene.[105] Patton, Lillya and McCarthy prepared cyclohexene oligomers at low temperature and showed that they depolymerized at room temperature in the presence of $WCl_6/SnMe_4$.[106] There is one example of cross metathesis of cyclohexene and ethylene to produce 1,7-cyclooctadiene under extremely high pressures of ethylene,[107-108] but under



Scheme 1.7. Metathesis of 1,3-COD to Yield Cyclohexene and Polyacetylene.

standard reaction conditions, cyclohexene should not be incorporated back into the polymer. Complete degradation of poly(1,3-COD) by backbiting reactions should result in equal moles of acetylene units in the polymer chain and free cyclohexene.

An intermediate degree of degradation of the polymer by metathesis carbenes should give copolymers of polyenes and cyclohexene. If the polymer was completely degraded to cyclohexene and PA, then the polyacetylene that resulted would not be any more tractable than that produced by the Shirakawa method discussed earlier. If we stopped the degradation at an intermediate stage and the degree of backbiting could be controlled, then copolymers with variable conjugation lengths would result, with corresponding changes in the processability of the material.

Metathesis degradation reactions (metathetical chain scission) offer a tremendous opportunity for the investigation of polymer microstructure and has been applied toward a number of different unsaturated polymers and networks, including several which were polymerized by non-metathesis mechanisms.[109] By controlling reaction conditions, complete digestion of a polymer into monomer units is possible, as shown by Korshak for the 100% conversion of poly(pentenamer) to cyclopentene.[110]

As a result of the negligible strain in six membered rings, cyclohexene rings are formed quite easily during metathesis reactions if the appropriate starting materials are present; a number of different examples have been reported. Cyclohexenyl products were observed in the metathesis degradation of dehydrodimers of 1,5,9-cyclododecatriene,[111] and the nearly complete disproportionation of octa-1,7-diene to cyclohexene and ethylene has been well documented.[112-114] Several authors have reported the degradation of polybutadiene to produce cyclohexene and cyclopentene,[115-117] and the degradation of poly(butadiene-*alt*-propene) copolymers to give substituted cyclohexenes.[118-119] Verkuijlen observed that significant amounts of cyclohexene were extruded in the degradation of linoleic and linolenic esters.[120] Cyclohexene was produced almost quantitatively (94%) in the metathesis polymerization of 1,5-cyclodecadiene and the *trans* content of the polymer increased over time.[121] The number and variety of examples of cyclohexene production via metathesis degradation showed that the degradation of poly(1,3-COD) into polyacetylene and cyclohexene was a reasonable goal.

1,3-COD had been traditionally known as poison for metathesis catalysts because the conjugated double bonds chelate to the metal in a bidentate fashion and block access to other monomers.[109,118] In fact, polybutadiene systems with large proportions of 1,2-blocks present were more difficult to degrade and required repeated catalysts additions. Despite these reports, Korshak reported the polymerization of 1,3-COD in 1981 and described the product as a rapidly crosslinking rubber-like substance with minimal air stability.[110] He did not allude to the production of any cyclohexene, but UV results showed shoulders at 265 and 300 nm on a broad band at 220 nm which he attributed to diene, triene and tetraene sequences. The formation of cyclic oligomers, including cyclohexene, could have resulted in the presence of extended conjugation in the chain.

Streck made thin films of poly(1,3-COD) by the base-catalyzed isomerization of poly(1,4-COD) and suggested the product as a quick drying replacement for tung oil.[122] Amass attempted the ROMP of 1,3-COD, but only got only a 5% yield of polymer.[123] They gave no details of the product characterization and did not show that the product resulted from ring-opening polymerization. Streck later reported that the presence of small amounts of 1,3-dienes, including 1,3-COD, in metathesis polymerizations promoted *cis*-selectivity without affecting the yield adversely.[124] Large amounts of 1,3-COD cut the yield but still had a positive effect on the *cis* content. To date, there has been extensive use of metathesis catalysts to degrade unsaturated systems into their low molecular weight components, but the studies detailed below actually used polymer degradation to design new materials.

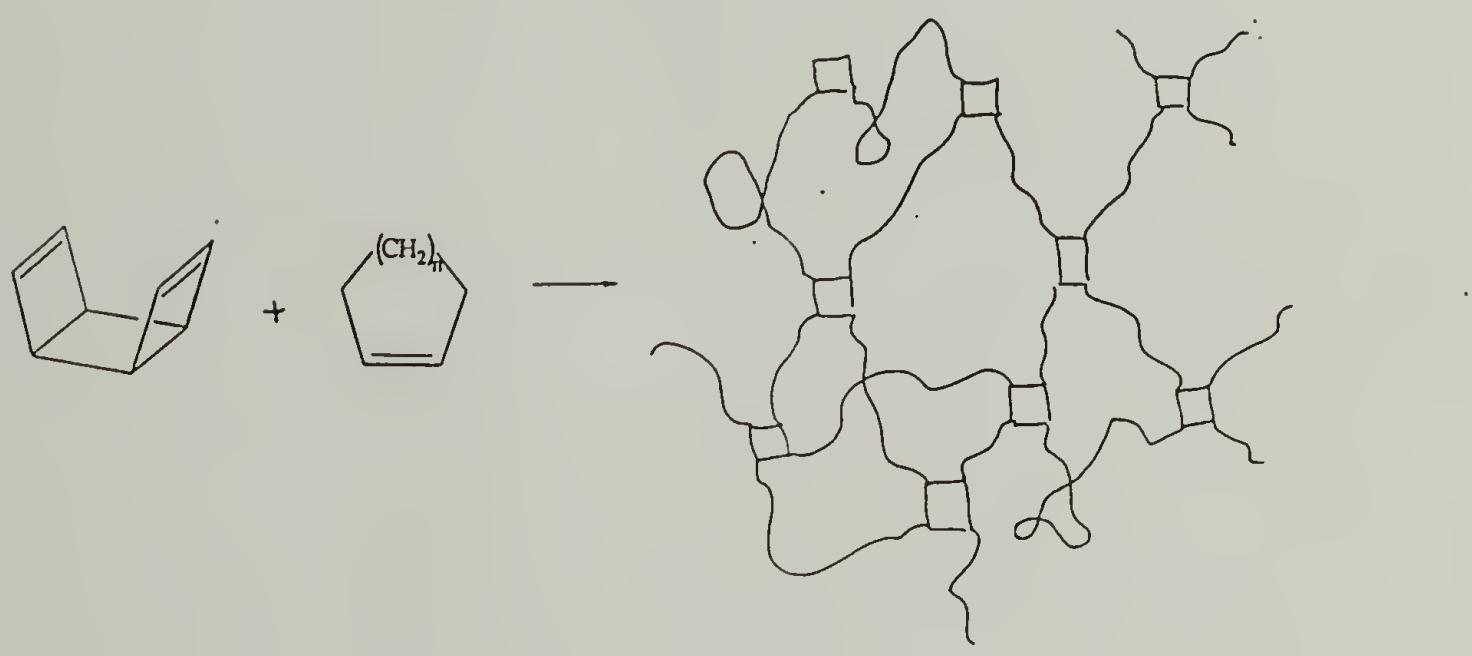
A Metathesis Crosslinking Agent

Our second investigation of applications of the metathesis reaction focused on the development of a crosslinking agent. In order to develop the potential of this reaction to function as a multifaceted method for designing new macromolecular structures, we need to develop the array of tools which are common to other types of polymerizations such as crosslinking agents, chain transfer agents, endcapping reagents and functionalized initiators. When our preliminary results were reported,[125] no crosslinking reagent had been developed for metathesis polymerizations, although some crosslinked products had been reported as a result of extraneous polymerization through other double or triple bonds in the molecule or via non-ring opening mechanisms. Recently, Schrock reported the use of the norbornadiene dimer to make crosslinked and star polymers.[126] With the alkylidene catalysts that he used, reactivity differences between monomers control the

types of olefins which can be used and the order by which they can be incorporated into block copolymers.

In this dissertation, we introduce syn-tricyclo[4.2.0.$0^{2,5}$]octa-3,7-diene (TCOD) as a metathesis crosslinking agent for polyalkenamer systems as depicted in Scheme 1.8. TCOD provides a crosslinking agent of a different reactivity, based on the difference in ring strain between the cyclobutene and cyclopentene rings in TCOD and the norbornadiene dimer, respectively. TCOD was chosen over other candidate tricyclic dienes because the synthesis was straightforward and because the ring strain of the four-membered rings should favor crosslinking at equilibrium.[127] We examined the homopolymerization of TCOD, as well as copolymerization in solution by two different routes with cyclooctene (COE) to form crosslinked networks. COE was chosen as a comonomer for the solution studies because it should have competitive metathesis rates with TCOD, yielding a random network. A set of solid samples with various concentration of the crosslinking agent present were also synthesized using the Hercules Metton™ catalyst system to test for differences in physical properties. In characterizing the potential of TCOD as a metathesis crosslinking agent, we employed the homogeneous $WCl_6/SnMe_4$ and WCl_6/Et_2AlCl catalyst systems, but expect that TCOD can be polymerized by a wide rage of metathesis catalysts. We wanted to exploit the versatile nature of TCOD as a crosslinking agent in order to prepare crosslinked polymer systems of varied functionality which are presently inaccessible. In addition, the ability to predetermine the crosslink density of a polymer provides us with a vehicle for custom tailoring networks.

Copolymerization of TCOD and a Generic Cyclic Olefin



Scheme 1.8. TCOD as a Tetrafunctional Crosslinking Agent.

References

1 Draguton, V.; Balabon, A. T.; Dinonie, M.; Olefin Metathesis and Ring-Opening Polymerization of Cyclo-Olefins, Wiley-Interscience, Chinchester, **1985**.

2. Ivin, K. J. Olefin Metathesis, Academic Press, London, **1983**.

3. Ivin, K. J.; Saegusa, T. Ring-Opening Polymerization, Elsevier, London **1984**. Vol. I.

4. Matejka, L.; Houtman, C.; Macosko, C. W. *J. Appl. Polym. Sci.* **1985**, *30*, 2787.

5. Streck, R. *J. Mol. Catal.* **1988**, *46*, 305.

6. Streck, R. *Chemtech* **1989**, 498.

7. Banks, R. L. *Catalysis* **1981**, *4*, 100.

8. Anderson, A. W.; Merckling, N. G.; **U. S. Pat.** 2 721 189 (1954/1955).

9. Eleuterio, H. S. **U. S. Pat.** 3 074 918, (1957).

10. Banks, R. L. *Chemtech* **1986**, *16*, 112.

11. Dall'Asta, G.; Mazzanti, G. *Makromol. Chem.* **1983**, *61*, 178.

12. Dall'Asta, G. *J. Polym. Sci. A-1* **1968**, *6*, 2397.

13. Natta, G.; Dall'Asta, G.; Mazzanti, G. *Angew. Chem.* **1964**, *76*, 765.

14. Calderon, N.; Chen H. Y.; Scott, K. W. *Tetrahedron Lett.* **1967**, 3327.

15. Scott, K. W.; Calderon, N.; Ofstead, E. A.; Judy W. A.; Ward, J. P. *Adv. Chem. Ser.* **1969**, *91*, 399.

16. Bradshaw, C. P. C.; Howman, E. J.; Turner, L. *J. Catal.* **1967**, *7*, 269.

17. Herrison, J. L.; Chauvin, Y. *Makromol. Chem.* **1970**, *141*, 161.

18. Katz, T. J.; McGinnis, J. *J. Am. Chem. Soc.* **1977**, *99*, 1903.

19. Schrock, R. R. *J. Am. Chem. Soc.* **1974**, *96*, 6796.

20. Schrock, R. R. *J. Am. Chem. Soc.* **1976**, *98*, 5399.

21. Howard, T. R.; Lee, J. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 6878.

22. Hughes, W. B. *Chemtech* **1975**, 486.

23. Ivin, K. J. Olefin Metathesis, Academic Press, London, **1983**. p. 326.

24. Boelhouwer, C. *J. Mol. Catal.* **1988**, *46*, 297.

25. Banasiak, D. S. *J. Mol. Catal.* **1985**, *28*, 107.

26. Streck, R. *J. Mol. Catal.* **1982**, *15*, 3.

27. Klosiewicz, D. W. **U.S. Patent** 4,400,340 (1983).

28. Mocella, M. T.; Busch, M. A.; Muetterties, E. L. *J. Am. Chem. Soc.* **1976**, *97*, 1283.

29. Casey, C. P.; Hornung, N. L.; Kosar, W. P. *J. Am. Chem. Soc.* **1987**, *109*, 4908.

30. Chien, J. C.W. Polyacetylene, Academic, Orlando Fla, 1984.

31. Shirakawa, H.; Ikeda, S. *Polymer J.* **1971**, *2*, 231.

32. Alimuniar, A. B.; Edwards, J. H.; Feast, W. J. *J. Mol. Catal.* **1985**, *28*, 313.

33. Ito, T.; Shirakawa, H.; Ikeda, S. *J. Polym. Sci. Polym. Chem. Ed.* **1974**, *12*, 11.

34. Korshak, Y. V.; Korshak, V. V.; Kanischka, G. Hocker, H. *Makromol. Chem. Rapid Comm.* **1985**, *6*, 685.

35. Edwards, J. H.; Feast, W. J. *Polymer* **1980**, *21*, 595.

36. Klavetter, F. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 7807.

37. Gorman, C.; Ginsberg, E.; Marder, S.; Grubbs, R. *Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem.* **1990**, 386.

38. Swager, T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 894.

39. Feast, W. J. *Synth. Met.* **1986**, *14*, 245.

40. Edwards, J. H.; Feast, W. J.; Bott, D. C. *Polymer* **1984**, *25*, 395.

41. Feast, W. J.; Wilson, B. *J. Mol. Catal.* **1980**, *8*, 277.

42. Feast, W. J.; Wilson, B. *Polymer* **1979**, *20*, 1182.

43. Blackmore, P. M.; Feast, J. W. *J. Mol. Catal.* **1986**, *36*, 145.

44. Stelzer, F.; Brunthaler, J. K.; Leising, G.; Hummel, K. *J. Mol. Catal.* **1986**, 36, 135.

45. Schrock, R. R.; Krouse, S. A.; Knoll, K.; Feldman, J.; Murdzek, J. S.; Yang, D. C. *J. Mol. Catal.* **1988**, *46*, 243.

46. MacDiarmid, A. G. *Solid State Commun.* **1978**, *27*, 489.

47. Leising, G.; Uitz, R.; Ankele, B.; Ottinger, W., Stelzer, F. *Molec. Crys., Liq. Crys.* **1985**, *117*, 327.

48. Bott, D. C.; Brown, C. S.; Edwards, S. H.; Feast, W. J.; Parker, D.; Winter, J. N. *Molec. Crys., Liq. Crys.* **1985**, *117*, 9.

49. Leising, G. *Polymer Comm.* **1984**, *25*, 201.

50. Dall'Asta, G. *Makromol. Chem.* **1962**, *56*, 224.

51. Ivin, K. J. Olefin Metathesis, Academic Press, London, 1983. p.224.

52. Katz, T. J.; Lee, S. J.; Shippey, M. A. *J. Mol. Catal.* **1980**, *8*, 219.

53. Kormer, V. A.; Dolinskaya, E. R.; Khatchaturov, A. S. *Makromol. Chem., Rapid Commun.* **1980**, *1*, 531.

54. Pettit, R. *Org. Syn.*, **1970**, *50*, 36.

55. Paquette L. A.; Carmody M. J. *J. Am. Chem. Soc.* **1976**, *98* , 8175.

56. Avram, M.; Marica, E.; Dinulescu, I.; Farcasiu, M.; Elian, M.; Mateescu, G.; Nenitzescu C. D. *Chem. Ber.* **1964**, *97*, 383.

57. March, J. Advanced Organic Chemistry, Wiley-Interscience, New York, **1985**, 3rd ed. p. 914, 924.

58. Brunthaler, J. K.; Stelzer, F.; Leising, G. *J. Mol. Catal.* **1985**, *28*, 393.

59. Wiberg, K. B.; Williams, V.Z.; Fredrich, L.E. *J. Am. Chem. Soc.* **1970**, *92*, 564.

60. Cope, A.C.; Schaeren, S. F.; Trumbull, E. R. *J. Am. Chem. Soc.* **1954**, *76*, 1096.

61. Cope, A.C.; Tiffany, B. D. *J. Am. Chem. Soc.* **1951**, *73*, 4158.

62. Depuy, C. H.; King, R. W. *Chem Rev.* **1960**, *60*, 431.

63. Van Dam, P. B.; Mittelmeijer, M.C.; Boelhouwer, C. *Chem. Commun.* **1972**, 1221.

64. Reyx, D.; Campistron, I.; Hamza, M. *J. Mol. Catal.* **1986**, *36*, 101.

65. Reyx, D.; Campistron, I.; Heiling, P. *Makromol. Chem.* **1982**, *183*, 173.

66. Ast, W.; Rheinwald, G.; Kerber, R. *Makromol. Chem.* **1976**, *177*, 1349.

67. Dodd, H. T.; Rutt, K. J. *J. Mol. Catal.* **1982**, *15*,103.

68. Reyx, D. *J. Mol. Catal.* **1980**, *8*, 325.

69. Mol, J. C. *J. Mol. Catal.* **1982**, *15*, 35.

70. Levisalles, J.; Villeman, D. *Tetrahedron* **1980**, *36*, 3181.

71. Ast, W.; Rheinwald, G.; Kerber, R. *Rec. Trav. Chim. Pays-Bas* **1977**, *96*, M127.

72. Nouguier, R.; Mutin, R.; Laval, J. P.; Chapelet, G.; Basset, J.; Lattes, A. *Rec. Trav. Chim. Pays-Bas* **1977**, *96*, M91.

73. Reyx, D.; Croissandeau, M. *Makromol. Chem.* **1982**, *183*, 1371.

74. Feast, J.; Harper, K. *J. Mol. Catal.* **1985**, *28*, 293.

75. Reyx, D.; Hamza, M.; Campistron, I. *J. Mol. Catal.* **1987**, *42*, 289.

76. Bianchini, C.; Meli, A.; Vizza, F. *Angew. Chem. Int. Ed.* **1987**, *26*, 767.

77. Otton, J.; Colleuille , Y.; Varagnat, J. *J. Mol. Catal.* **1980**, *8*, 313.

78. Mol, J. C. *Chem. Commun.* **1981**, 1132.

79. Mol, J. C. *Chemtech* **1983**, *13*, 250.

80. Thu, T.C.; Bastelburger, T.; Hocker, H. *J. Mol. Catal.* **1985**, *28*, 279.

81. Grubbs, R.H., in Compendium of Organometallic Chemistry, Wilkenson, G.; Stone, F. G. A.; Asbel, E. W. Eds.; Pergamon Press, Ltd.; Oxford, **1982**; Vol. 8, p. 499.

82. Verluijlen, E.; Dirks, R. J.; Boelhouwer, C. *Rec. Trav. Chim. Pays-Bas* **1977**, *96*, M86.

83. Mol, J.C.; Woerlee, E. F. G. *Chem. Commun.* **1979**, 330.

84. Castner, K. F.; Calderon, N. *J. Mol. Catal.* **1982**, *15*, 47.

85. Patton, P.A.; McCarthy, T.J. *Macromolecules* **1987**, *20*, 778.

86. F. Stelzer, C. Grainmann and K. Hummel, *Colloid Polym Sci.* **1982**, *260*, 829.

87. Ho, H.T.; Ivin, K. J.; Rooney, R. R. *J. Mol. Catal.* **1982**, *15*, 245.

88. Ivin, K. J.; Milligan, B. D. *Makromol. Rev.* **1987**, *8*, 269.

89. Ivin, K. J. Olefin Metathesis, Academic Press, London, **1983**, p.309.

90. Thoi, H. H.; Reddy, B. S. R.; Rooney, J. J. *J. Chem Soc., Faraday Trans. I* **1982**, *78*, 3307.

91. El Saafin, I. F.; Feast, J. W. *J. Mol. Catal.* **1982**, *15*, 61.

92. Mol, J. C. *J. Chem. Therm.* **1983**, *15*, 147.

93. Mol, J. C.; Moulijn, J. A. *Adv. Catal.* **1975**, *24*, 131.

94. Ellison, A.; Coverdale, A. K.; Dearing, P. F. *J. Mol. Catal.* **1985**, *28*, 141.

95. Verkuijlen, E.; Kapteijn, F.; Mol, J. C.; Boelhouwer, C. *Chem. Commun.* **1977**, 198.

96. Nakamura, R.; Matsumoto, S. *Chem. Lett.* **1976**, 1019.

97. Olsthoorn, A. A.; Boelhouwer, C. *J. Catal.* **1976**, *44*, 207.

98. Xiaoding, X.; Andreini, A.; Mol, J. C. *J. Mol. Catal.* **1985**, *28*, 133.

99. Mol, J. C. *J. Chem. Therm.* **1983**, *15*, 137.

100. Ellison, A.; Coverdale, A. K.; Dearing, P. F. *Applied Catal.* **1983**, *8*, 109.

101. Moulijn, J. A. *J. Mol. Catal.* **1985**, *30*, 111.

102. Nakamura, R.; Echigoya, E. *Rec. Trav. Chim. Pays-Bas* **1977**, *96*, M31.

103. Mol, J. C. *Rec. Trav. Chim. Pays-Bas* **1977**, *96*, M139.

104. Yide, X.; Xinguang, W.; Yingzhen, S.; Yihua, Z.; Xiexian, G. *J. Mol. Catal.* **1986**, *36*, 79.

105. Odian, G. Principles of Polymerization, Wiley-Interscience, New York, **1985**. 2nd Ed., p. 268.

106. Patton, P.A.; Lillya, C. P.; McCarthy, T.J. *Macromolecules* **1986**, *19*, 1266.

107. Crain, D. L., **U.S. Patent** 3 575 947 (1971).

108. Crain, D. L.; Reusser, R. E. *Prepr. Am. Chem. Soc., Div. Pet. Chem.*, **1972**, *17*, E80.

109. Thorn-Csanyi, E.; Perner, H. *J. Mol. Catal.* **1986**, *36*, 187.

110. Korshak, Y. V.; Tlenkopatchev, M.A.; Dolgoplosk, B. A.; Avdeikina, E. G.; Kutepov, D. F. *J. Mol. Catal.* **1982**, *15*, 207.

111. Hummel, K.; Lechner, H.; Pongratz, T. *J. Mol. Catal.* **1986**, *36*, 177.

112. Zuech, E. A.; Hughes, W. B.; Kubicek, D. H.; Kittleman, E. T. *J. Am. Chem. Soc.* **1970**, *92*, 528.

113. Hughes, W. B. *J. Am. Chem. Soc.* **1970**, *92*, 532.

114. Doyle, G. *J. Catal.* **1973**, *30*, 118.

115. Canjii, E.; Abenrothm H. *Makromol. Chem.* **1975**, *176*, 775.

116. Heiling, P.; Honig, H.; Hummel, K. *Monatsh. Chem.* **1980**, *111*, 575.

117. Hummel, K.; Chemelli, R.; Griefer, H.; Kumar, V. N.; Stelzer, F., *Makromol. Chem. Rapid Comm.* **1983**, *4*, 429.

118. Korshak, Y. V.; Dolgoplosk, B. A.; Tlenkopachev, M. A. *Rec. Trav. Chim. Pays-Bas* **1977**, *96*, M64.

119. Hummel, K.; Lechner, H.; Zekoll, H.; Chemelli, R. *Makromol. Chem.* **1987**, *188*, 1075.

120. Verkuijlen, E.; Boelhouwer, C. *Chem. Commun.* **1974**, 793.

121. Hocks, L.; Berck, D.; Hubert, A. J.; Teyssie, P. *J. Polym. Sci., Polym. Lett. Ed.* **1975**, *13*, 391.

122. Holtrup, W.; Streck, R.; Zaar, W.; Zerpner, D. *J. Mol. Catal.* **1986**, *36*, 127.

123. Amass, A. J.; McGourtey, T. A.; Tuck, C. N. *Eur. Polym. J.* **1976**, *12*, 93.

124. Zerpner, D.; Holtrup, W.; Streck, R. *J. Mol. Catal.* **1986**, *36*, 153.

125. Coleman, C.G.; McCarthy, T.J. *Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem.* **1988**, 29(1), 283.

126. Schrock, R. R.; Bazan. G. *Macromolecules, in press.*

127. Patton, P.A.; McCarthy, T.J. *Macromolecules* **1984**, *17*, 2939.

CHAPTER 2

EXPERIMENTAL

Materials and Methods

Laboratory Equipment

Reaction tubes. The majority of the metathesis reactions were run in custom made flasks from the University of Massachusetts glass shop. The tubes are referred to generically as Schlenk tubes, and some of the basic designs are shown in Fig. 2.1. The tubes were connected to nitrogen and vacuum via 14/20 female joints in series with 4 mm teflon stopcocks in either side-arm or tube-top configurations. Either ground glass (28/34 or 24/40) or o-ring(#25) joints were used to connect tube tops and bottoms. O-ring tubes were held together with metal clamps; lycra proved invaluable for holding the larger ground glass jointed reaction tubes together under positive pressure. When possible, tubes with ground glass joints were used for long duration reactions, but both types were used for short term, room temperature reactions.

Storage Flasks. Storage flasks were used to store solvents and reagents which had been purified and required inert atmosphere storage. As shown in Fig 2.1, storage flasks consisted of round bottomed flasks or oblong tubes of various sizes (5-1000 mL) sealed with 4 mm teflon stopcocks. An extra "handle" was attached to the larger flasks as a more convenient clamping appendage. Ground glass joints (14/20) in series with the stopcocks connected the flasks to the vacuum line directly, or rubber septa were used to seal the joints for needle access. Individual stopcocks were labeled and kept with specific storage tubes as much as possible to prevent leakage and to insure stopcock compatibility. Graduated storage tubes were made by substituting 15 mL centrifuge tubes (0.1 mL

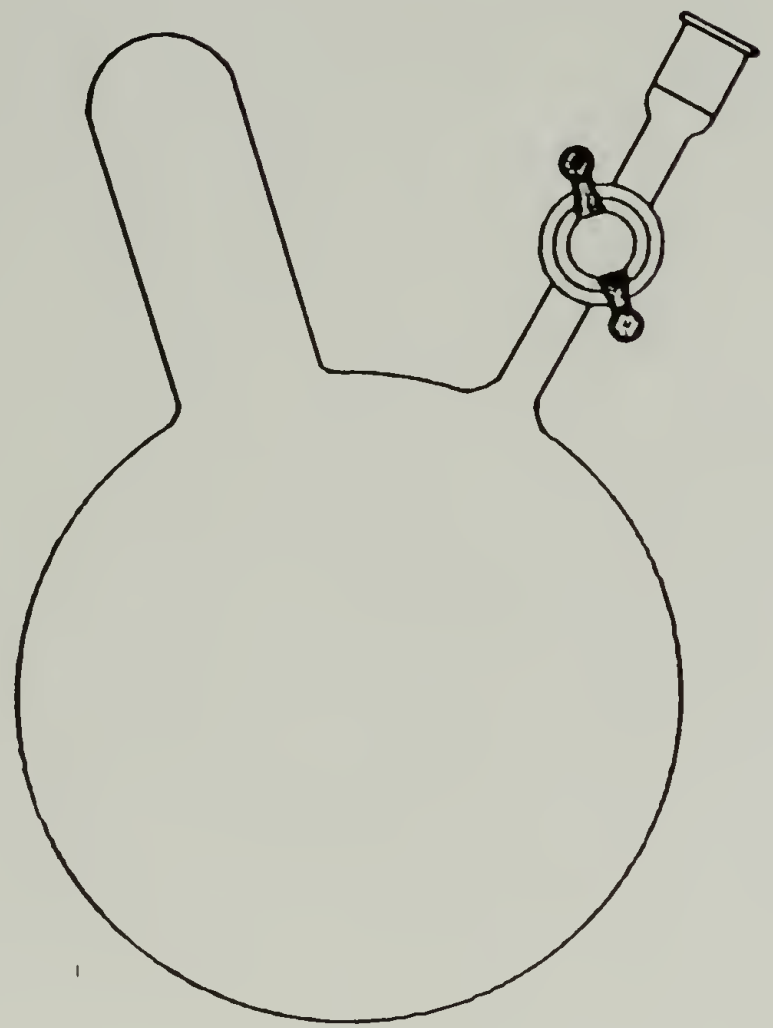
graduations) for the round bottomed flasks. The graduations on these tubes were used to measure out reagents in some cases when accuracy of ±0.1 mL was acceptable, so that transfers could be made directly via cannula. Lycra or copper wire was used to seal rubber septa around ground glass joints.

Distillations. Several types of distillations were run for these studies. A standard still head was used for distilling large quantities of solvents away from solid drying agents. For drying small volumes of reagents (less than 50 mL) or for distilling mixtures with differences in boiling point between components greater than 100°C, a trap-to-trap apparatus was used. Continuous stills were used for distilling frequently used solvents like chlorobenzene. Both types of still are shown in Fig. 2.2. Small quantities were also distilled using a short path "pig still" as purchased from Ace Glass. When boiling point differences were relatively small, a Perkin Elmer Auto Annular Still (Model 254) was used to perform spinning band distillations. This model was equipped with a 36" teflon band and an adjustable rate takeoff valve. Hold-up volume was 0.5 mL, making it possible to distill relatively small amounts of material.

Vacuum System. A glass vacuum manifold (Figure 2.3) with four ports to vacuum and direct nitrogen access on several ports was used for all experiments. Full vacuum for this system registered 0.02 mm on a calibrated thermocouple gauge.

Instrumentation and Analysis

GC analysis was carried on a Hewlett Packard 5790 GC. Varian 200 and 300 MHz instruments were used for NMR analysis with chloroform(-d_1) and benzene(-d_6) as NMR solvents. A Manowatch (I^2R™) was used to regulate vacuum distillations. A Haake recirculation bath was used to control condenser temperatures in some distillations and Gel Permeation Chromatography was carried out with a Rainin instrument, using PL-gel columns obtained from Polymer Laboratories and a refractive index detector.



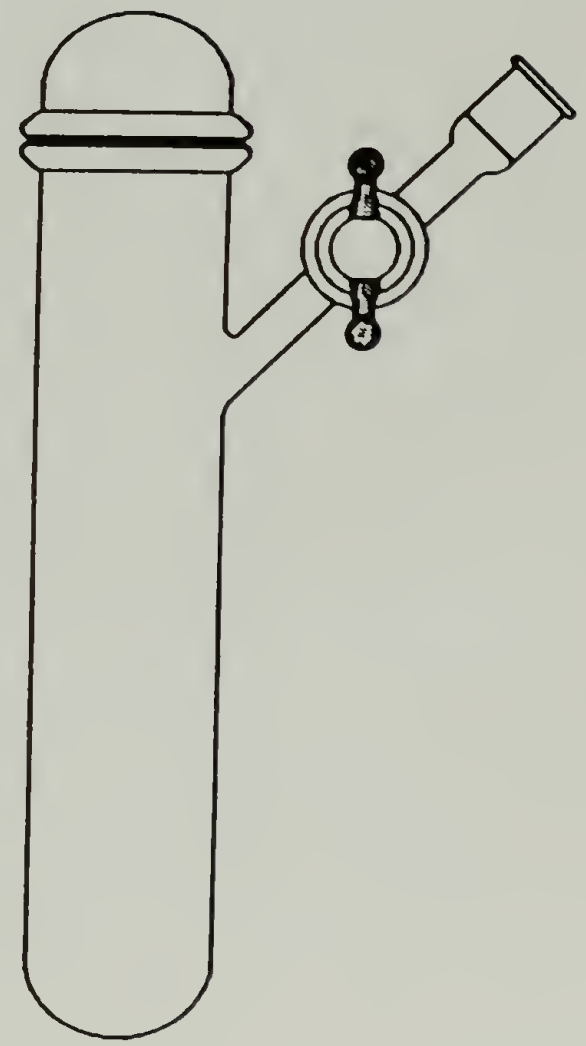


Figure 2.1. Schlenk Tube and Storage Flask Diagrams.[1]

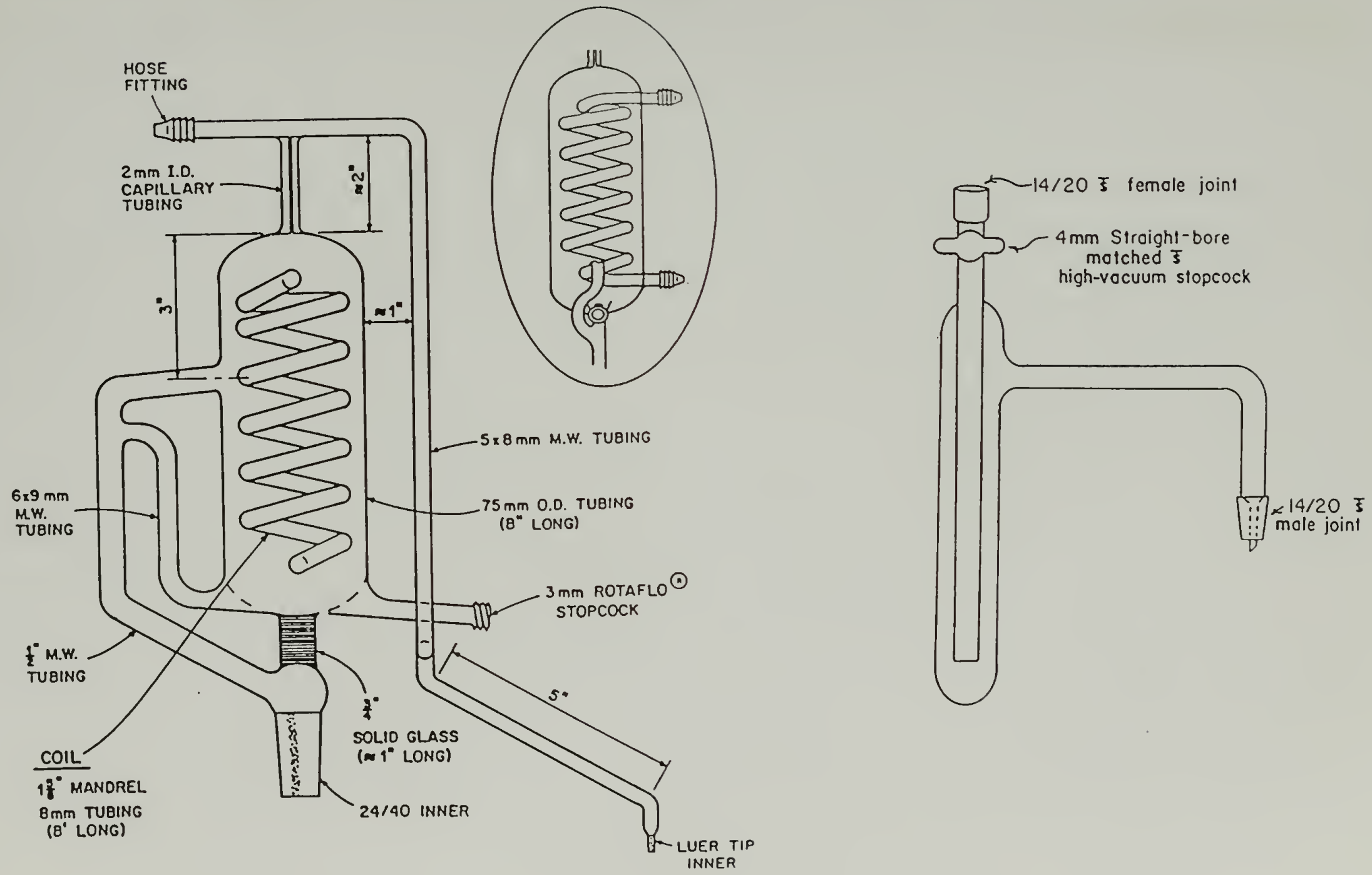


Figure 2.2 Distillation Glassware.

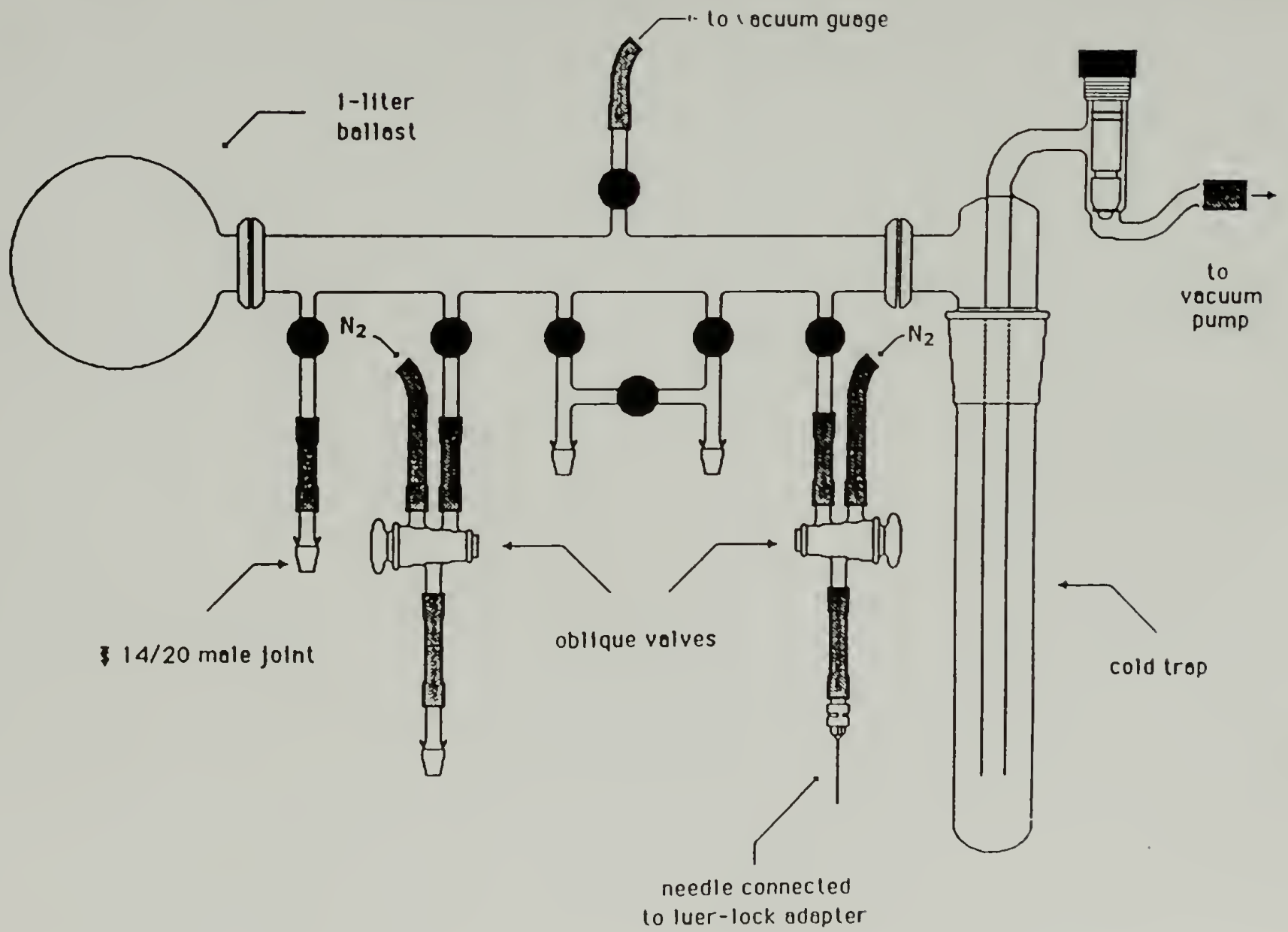


Figure 2.3 Glass Vacuum Manifold.

Materials

All chemicals were reagent grade unless otherwise noted. DCCB was purchased from Fluka Chemical. Ammonium perrhenate (NH_4ReO_4) 99% was obtained from Alfa and γ-Al_2O_3 was purchased from Aesar. General use solvents such as diethylether (Et_2O), tetrahydrofuran (THF), methylene chloride ($MeCl_2$), and acetone were purchased from Fisher or Aldrich and were reagent grade unless otherwise noted. Norbornene (NBE, 99%), 1,3-cyclooctadiene (1,3-COD, 98%), 1,5-cyclooctadiene (1,5-COD, 99%) cyclooctene (COE), decane, WCl_6 (Gold Label), $EtAlCl_2$, nonane, chlorobenzene, cyclohexene, heptane, octane, $SnMe_4$ were purchased from Aldrich and used as received, unless noted otherwise.

General Notes for Metathesis Reactions

All air sensitive reagents were handled according to standard procedures.[2] Unless otherwise noted, all metathesis reactions were run under a nitrogen atmosphere, and all liquids were transferred via cannula or syringe. Solvents and reagents were dried over CaH_2 and distilled with either standard still heads or a trap-to-trap apparatus. Catalyst solutions were made up with chlorobenzene as the solvent. Heptane, nonane and decane were employed as internal standards for metathesis polymerizations. These were stirred over H_2SO_4, washed with water, predried over $MgSO_4$ and distilled from CaH_2. Catalyst solutions were tested using 1,5-COD or COE as monomers in trial polymerizations either at the same time or directly preceding the experimental polymerizations.

Monitoring Polymerizations by Gas Chromatography

Most polymerizations described in this section were monitored using gas chromatography. Depending on the specific combination of monomers and internal standards (IS) in each system, the AN600, OV101, DC200 or SuperPak II columns

were used, as specified in the individual studies. For most polymerizations, the ratio of monomer to an IS was measured before combination with the catalyst, and then aliquots (~0.1 mL) were removed periodically via cannula to measure the concentration of the monomer, relative to the internal standard. Several microliters of water were added to each aliquot to prevent further polymerization and to precipitate most of the high polymer formed. The addition of water to GC samples did not affect the relative amounts of reaction components for these reactions. The most consistent data was obtained when the standard was present in approximately the same quantity as the monomer. Using this method, differences in the quantities of each monomer present could be obtained, relative to other reactions involving the same monomer and internal standard. A sample calculation is shown in Scheme 2.1..

Ratio of Monomer to Internal Standard = M_0/Std = R_0
Ratio of Monomer to Internal Standard at Time (t) = M_t/Std = R_t
Relative Amount of Monomer Remaining = R_t / R_0

Example: R_0= 0.80, R_t= 0.60 R_t / R_0 = 0.75
75% of Monomer is still in solution

Scheme 2.1. Calculation of Percent Monomer Remaining by GC.

Notebook References

Notebooks are designated chronologically by roman numerals, followed by the specific page numbers in arabic numerals. For example, III-45 refers to page 45 of the third notebook.

Catalyst Systems

$WCl_6/SnMe_4$

The $WCl_6/SnMe_4$ catalyst system was chosen for its compatibility with a variety of functional groups, including halogens and esters which were of special interest in these studies. In addition, a homogeneous system would simplify quantitative analysis, because the polymers formed in these studies have potential solubility problems.

Tungsten Hexachloride. Solutions of WCl_6 in chlorobenzene were made from fresh vials of WCl_6. The vial was scored and then placed in a glove bag with a stir bar, a rubber septum and a 300 mL 24/40 1N-RB flask which had been tared. After measuring the approximate amount of WCl_6 into the flask, the septum was placed over the joint and the flask brought out into the air. After being weighed, the flask was placed under nitrogen and the septum was wired down. The correct amount of freshly distilled chlorobenzene to make up the desired concentration was transferred under nitrogen directly from a continuous still into a septum-sealed graduated cylinder, then transferred via cannula into the flask with the catalyst. After stirring for several hours under a positive pressure of nitrogen, the catalyst solution was transferred via cannula to a 100 mL storage flask.

Tetramethyltin. $SnMe_4$ was purchased from Aldrich Chemical, distilled trap-to-trap from CaH_2 and transferred via cannula into a storage flask. Stock solutions were made up by transferring $SnMe_4$ via syringe into a 15 mL graduated storage tube and then diluting to a specific volume with freshly distilled chlorobenzene.

Stoichiometry. Literature reports site ratios of WCl_6 to $SnMe_4$ for this catalyst ranging from 1/1 to 1/7.[34] In the experiments described here, a ratio of 1:2 was generally used, because preliminary studies in our laboratory indicated that this ratio worked well

over a variety of initiation conditions.[5] The ratio of monomer to tungsten varied from 12:1 to 500:1, depending on the specific requirements of the experiment.

Metathesis Polymerization Procedures for $WCl_6/SnMe_4$. The three general polymerization methods (A, B, C) were developed for use with the $WCl_6/SnMe_4$ catalyst system. Specific modifications, if applicable, are described with the individual studies.

Homopolymerization Method A. The tin and tungsten components were combined and allowed to age before adding the monomer: In a typical polymerization, 1.0 mL of $SnMe_4$ solution (0.2 M in chlorobenzene) was transferred via cannula or syringe from a 15 mL graduated storage tube into a reaction tube which had either been purged with copious amounts of nitrogen or flushed with nitrogen and evacuated at least three times. An equal volume of WCl_6 solution (0.1 M in chlorobenzene) was added via syringe and the catalyst was aged, typically for 20 minutes, before adding a composite solution of monomer and internal standard (sometimes diluted with the reaction solvent) via cannula or syringe. With this system, red to brown colors were indicative of a healthy catalyst and green or blue colored solutions did not usually result in significant decreases in the quantities of monomer present.

Homopolymerizations Method B. The $SnMe_4$ solution was added to a composite solution of the monomer and tungsten: For some experiments it was convenient to add the $SnMe_4$ component after combining the monomer and WCl_6 solutions. Although WCl_6 alone has been known to catalyze metathesis reactions,[6] the uncertainty regarding the true initiation time for the reaction was not a concern for reactions where the main objective was to convert monomer to polymer. The desired amount of WCl_6 solution was added to a reaction flask, followed by the monomer. At t=0, the $SnMe_4$ solution was added. Reaction colors were usually the same as for the combined reaction mixtures using

Method A. The solution containing monomer and WCl_6 was purple colored, turning to the familiar red-brown when the tin solution was added.

Homopolymerization Method C. Extra portions of WCl_6 and $SnMe_4$ were added to polymerizations: Because the goal in some experiments was to maximize the conversion of monomer to polymer, additional portions of WCl_6 and $SnMe_4$ were added over the course of the reaction to insure that active catalyst species were available to the monomers. Method C (12 h, 24 h) would refer to a reaction where additional portions of catalyst were added at the 12 and 24 hour points. The reactants were initially combined using method A with a 20 min aging period.

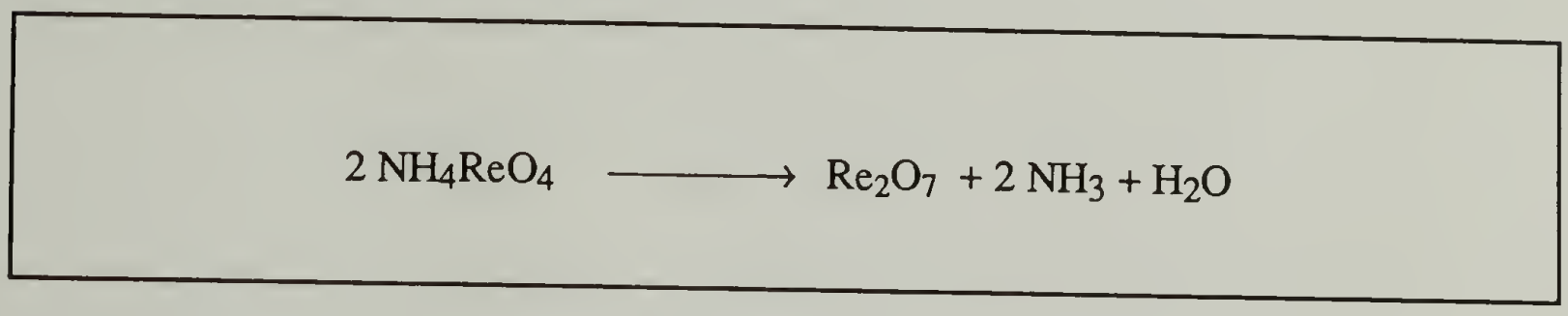
Catalyst Testing. In most cases, a trial polymerization of 1,5-cyclooctadiene (1,5-COD) was used to test the activity of the catalyst. If addition of 1,5-COD to the mixture of $WCl_6/SnMe_4$ produced a red-brown color indicating a healthy catalyst, then the experiment was continued by adding the appropriate monomer to a second flask containing catalyst.

Copolymerization Type I. The first monomer was added to the catalyst mixture after the appropriate aging period and then the second monomer was added at a later point to observe the effect on the rate of polymerization of the first monomer. GC samples were taken before and after the addition of the second monomer to measure the effect of the second type of carbene species on the polymerization rate.

Copolymerizations Type II. Both monomers were added simultaneously to the catalyst mixture after the appropriate aging period, and the rate of disappearance of both from solution was monitored. Chain transfer agents were also used in some of these studies to control molecular weight.

$Re_2O_7/SnMe_4/Al_2O_3$

$Re_2O_7/SnMe_4/Al_2O_3$ is a heterogeneous catalyst system known for its compatibility with functional group-containing olefins. It was used in polymerization studies with DCCB to avoid some of the side reactions encountered with the $WCl_6/SnMe_4$ system. To prepare this catalyst, γ-Al_2O_3 was impregnated with an aqueous solution of ammonium perrhenate (NH_4ReO_4) and then calcined at 550°C to produce Re_2O_7/Al_2O_3, as shown in Scheme 2.2. Solutions of a cocatalyst ($SnMe_4$) were added before polymerization to form the active species.



Scheme 2.2. Formation of Re_2O_7 from NH_4ReO_4.

Re_2O_7 Catalyst Preparation. Preparation (IV-7, 8, 9, 11) of $Re_2O_7/SnMe_4/Al_2O_3$ (15% by weight) and metathesis reaction conditions were modeled after those described by Mol.[7]

Impregnation. Ammonium perrhenate (NH_4ReO_4, 0.840 g) was dissolved with stirring in 25 mL H_2O. This solution was slurried with 4.25 g of γ-Al_2O_3 in a 1N-RB flask, and then most of the water was distilled off using a short path still. The remaining water was removed under vacuum (0.05 mm/12 h). The lumpy white solid was crushed to a fine powder using a mortar and pestle and transferred via funnel into a 36" quartz tube. The tube was 1" in diameter and had a 14/20 male joint at one end and a gas inlet at

the other. The tube had been plugged with quartz wool at one end before introducing the alumina in order to make it easier to confine the powder to the furnace area. The tube was placed in the furnace and was connected to a bubbler in the hood with a female 14/20 joint and tygon tubing.

Calcination. The catalyst was calcined at 550°C in the preheated tube furnace for three hours in air and then for one hour in nitrogen. The air had been dried through a 1.5" x 12" column of 3Å molecular sieves before reaching the tube furnace. The first 20 min of calcination produced a vigorous reaction as evidenced by the quantity of gas passing through the bubbler. After gas evolution slowed, the gas flow over the catalyst was reduced to 20 bubbles per minute. The color of the resultant catalyst ranged from pure white to carbon black, depending on the amount of water left in the Al_2O_3 at the start of the calcination workup. Alumina which had been completely dried under vacuum after NH_4ReO_4 impregnation remained white.

Al_2O_3 "Control" Catalyst. To evaluate the performance of the $Re_2O_7/SnMe_4/Al_2O_3$ catalyst, a control was needed to ascertain the effect of γ-Al_2O_3 alone on the amount of monomer left in solution after the polymerizations. This catalyst was prepared using the same procedure as outlined above, except that the water did not contain any NH_4ReO_4. Both the Re_2O_7 and control catalysts were transferred to Schlenk storage tubes using standard Schlenk techniques.

Metathesis Polymerization Procedures for $Re_2O_7/SnMe_4/Al_2O_3$. The stoichiometry used in these reactions was the same as that described by Mol.[7] Based on a 0.5 g scale (15% Re_2O_7/Al_2O_3), 36 mmoles of $SnMe_4$ was added to polymerize 0.25 g of a typical cyclic alkene monomer, resulting in a ratio of 20/1 (monomer to Re equivalents). Although the actual quantities of reagents in the individual polymerizations

were varied, the ratio of monomer to rhenium and the ratio of rhenium to tin remained constant.

Using the glove box, 0.5 g samples of 15% $Re_2O_7/\gamma\text{-}Al_2O_3$ were transferred from a Schlenk storage tube into #25 o-ring reaction tubes containing small stir bars. The tubes were clamped together, removed from the glove box and placed immediately under nitrogen. $SnMe_4$ solution was added via cannula and the slurry was well mixed before introducing the composite solution containing monomer and internal standard in chlorobenzene. If the reaction was at a temperature other than room temperature, then both the catalyst and monomer solutions were heated or cooled before being combined. 1,5-COD was used as a test monomer for the $Re_2O_7/SnMe_4$ system.

<u>WCl_6/Et_2AlCl Catalyst System</u>[8]

Synthesis of Solid Samples: Because the network samples were designed to be crosslinked and therefore insoluble, we needed a catalyst which could produce samples in solid form. Hercules used the two part Metton™ catalyst (WCl_6/Et_2AlCl) system to polymerize dicyclopentadiene in a Reaction Injection Molding (RIM) process to produce a high modulus thermoset material with exceptional impact strength. Macosko et. al.[9] published the procedure for polymerization of dicyclopentadiene (DCP) and norbornene (NBE) and using this as a model, we arrived at the following protocol for using the WCl_6/Et_2AlCl catalyst for the synthesis of solid samples to test the mechanical properties of the network polymers.

A solution of WCl_6 (0.07 M) was made up, following the standard procedures reported for the $WCl_6/SnMe_4$ system. Three equivalents of acetylacetone, which had been washed with 2 M NaOH and then distilled from P_2O_5, were added via syringe to a small round bottom flask. The flask contained three equivalents of *tert*-butylphenol and had been carefully flushed with nitrogen. The resulting solution was added to the WCl_6

solution to solubilize the WCl_6 and to extend the shelf life of the reagent. The mixture was purged with nitrogen for several hours to remove any HCl formed and the resulting reddish-purple colored solution, referred to as the tungsten component of the catalyst, was added to the monomer in a ratio of Monomer/WCl_6 = 1000/1. To prepare the alkylaluminium component of the catalyst, Et_2AlCl was added via syringe to the monomer in a ratio of Monomer/Et_2AlCl = 150/1, along with four equivalents (based on Et_2AlCl) of *n*-butylether which had been dried over CaH_2. The ether acts as a moderator for the polymerization and provides an induction period.

In a typical experiment, two equal portions of monomer, each containing one of the two catalyst components, was transferred via cannula or syringe to an appropriate reaction vessel for mixing. The resulting stoichiometry was as follows:

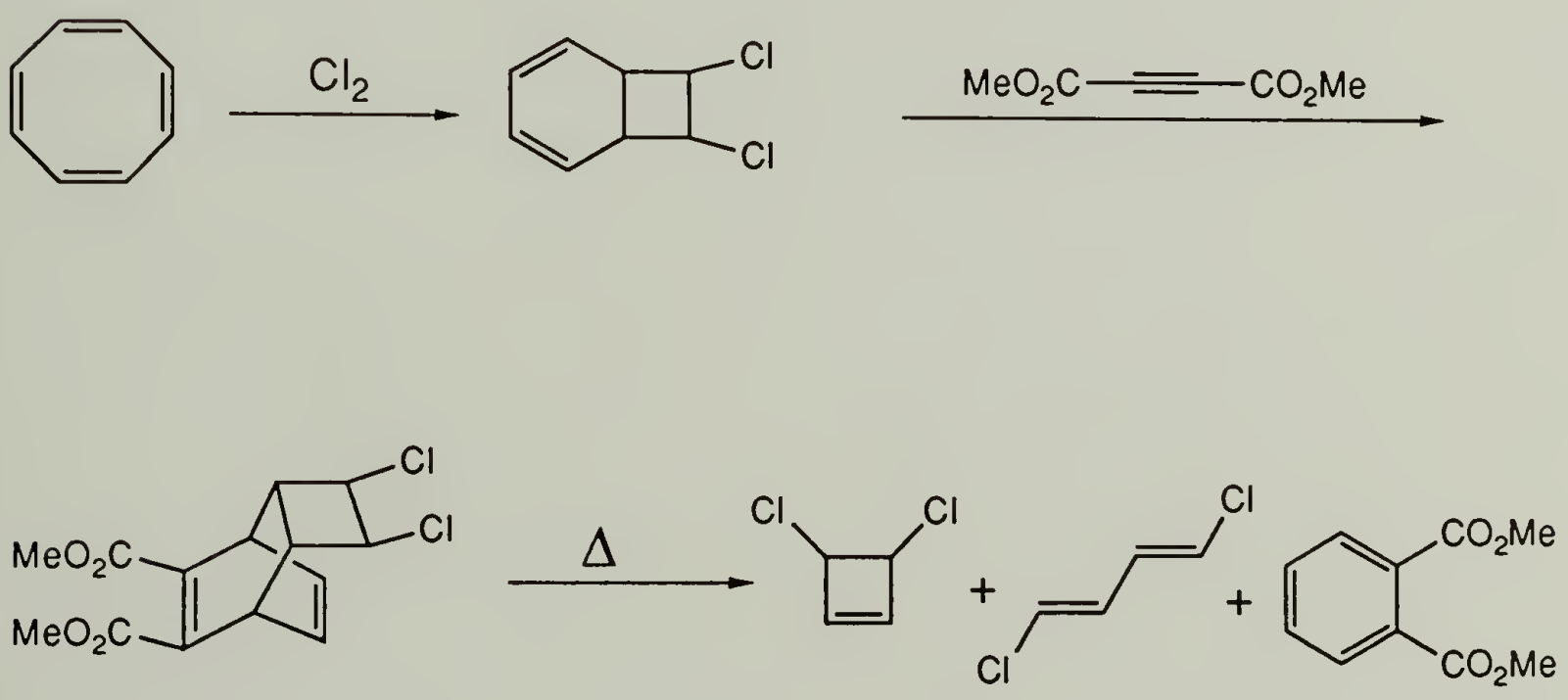
Monomer/WCl_6 = 2000/1	Acetylacetone/Phenol/WCl_6 = 3/3/1
Monomer/Et_2AlCl = 300/1	Et_2AlCl/*n*-butylether = 1/4

For the initial polymerization trials to determine the best monomer and sample configuration for this series of samples, the volume of the solutions was measured by eye. After the two components were combined, there was a short induction period of 30-60 seconds, depending on the amount of *n*-butylether present. The polymerization was rapid (~10 seconds for 2-4 mL samples) once it started and quite exothermic. It could be followed by eye because the monomer solution turned from a deep red to a brown color.

Metathesis Studies with *cis*-3,4-Dichlorocyclobutene

Monomer preparation

Some of the DCCB used in these metathesis studies was synthesized using Pettit's procedure from the Organic Synthesis Series,[10] as shown in Scheme 2.3. Details of the synthesis can be found in Notebook III. The remainder was purchased from Fluka (98% purity). The impurities present in DCCB from both sources included cyclooctatetraene (COT) and 1,4-dichlorobutadiene. COT was one of the starting materials for the synthesis and 1,4-dichlorobutadiene was the thermal decomposition product from any trans-3,4-dichlorocyclobutene present. *cis*-DCCB is more stable than the trans isomer, due to steric hindrance of the conrotatory motion necessary for thermal decomposition.



Scheme 2.3 Synthesis of 3,4-Dichlorocyclobutene.

Both 1,4-dichlorobutadiene and cyclooctatetraene could be separated from DCCB by distillation on a spinning band column, but the separation was not trivial because the butadiene isomer solidified in the condenser and along the path to the receiving flask. Even when a recirculation bath was used to keep the condenser temperature at 30-35°C, small amounts of the ring-opened impurity continued to wash down when pure DCCB distilled over. Unless otherwise noted, DCCB used in all metathesis experiments was ≥98% pure, as measured by GC.

Homopolymerization of DCCB with the $WCl_6/SnMe_4$ Catalyst System

Reaction conditions for the metathesis homopolymerization of DCCB (III-25, 27, 29, 31) are shown in Table 2.1. Unless otherwise noted, Method A with a 20 minute aging period was used, and reactions were monitored by GC periodically. Exact quantities of reagents and catalyst are listed in Notebook IV..

Homopolymerization of DCCB with the $Re_2O_7/SnMe_4/Al_2O_3$ Catalyst System

The $Re_2O_7/SnMe_4/Al_2O_3$ system was tested with 1,5-COD,[11] using the procedure detailed in the catalyst section (IV-15, 17). When a solution of the olefin in chlorobenzene was added to the catalyst (15% loading) at room temperature, the reaction mixture increased in viscosity and produced a rubbery white polymer after precipitation into methanol. The polymerizations of DCCB were also run using the procedure from the catalyst section with a DCCB/Re ratio of 20/1. DCCB (1.0 mL, 0.83 M) in chlorobenzene was added to each of two o-ring tubes. Tube A contained 0.14 g of 15% Re_2O_7/Al_2O_3 and Tube B contained the same amount of the control catalyst (plain alumina). $SnMe_4$ (0.036 mmoles) had been added to each tube before addition of the monomer and internal standard. After stirring 20 h, Tube A contained a fine black precipitate mixed in with the white alumina support and Tube B appeared unchanged.

Table 2.1 Metathesis Homopolymerization of DCCB with $WCl_6/SnMe_4$.

Reaction	W : Sn : Monomer	Temp °C	Monomer Consumed	Total Reaction Time (h)	Comments
III-25	1 : 1.5 : 16	25	12% 17% 100%	24.0 28.0 44.0	Additional catalyst added at 42.5h Ratio of W:Sn = 1:2
III-27	1 : 1.5 : 16	80	35% 42% 100%	9.5 11.0 18.0	Additional catalyst added at 15.5h Ratio of W:Sn = 1:1
III-29	1 : 2.2 : 200	80	4% 11%	7.0 19.0	No additional catalyst added, stopped sampling at 19.0 h
III-31	1 : 2.2 : 200	80	2%	0.5	Reaction mixture turned brown after 0.5h. Took several 2% samples.

Notes: Method was to add WCl_6 and $SnMe_4$ to tube, age 20 min, and then add DCCB.

1. Controls with 1,5-COD were done in which the 1,5-COD disappeared almost immediately, except in III-29 (no control)

2. GC conditions OV101, 10.2 min @70°C, 6.0 min @ 140°C. Retention times in minutes: Chlorobenzene 7.16, DCCB 8.96, decane 12.99 (Internal Standard).

GC showed that 17% of the DCCB originally present had been consumed, while 39% had disappeared from the control reaction in Tube B. In addition, a peak at the retention time of the ring-opened decomposition product showed up on the GC trace for the control reactions.

Copolymerization of DCCB with NBE with $Re_2O_7/SnMe_4/Al_2O_3$

Because the $Re_2O_7/SnMe_4/Al_2O_3$ system was up and running, the first copolymerizations were carried out with this heterogeneous system (IV-19, 21). The two monomers, internal standard, reaction solvent and any chain transfer agents were mixed prior to combination with the catalyst in a septum covered round bottom flask. For Type I copolymerizations, the monomer solution (NBE/DCCB=85/15) was added to the Re_2O_7/Al_2O_3 after it had been mixed with the appropriate amount of $SnMe_4$ in chlorobenzene.

Initial attempts at copolymerization were unsuccessful with this catalyst system. Even though both DCCB and the internal standard were very dilute, NBE disappeared in these reactions, and the concentration of DCCB did not change noticeably. High molecular weight NBE precipitated out of solution despite the presence of *cis*-2-hexene as a chain transfer reagent and lower reaction temperatures. These difficulties stemmed from the heterogeneous nature of the catalyst system and we turned our efforts to the homogeneous $WCl_6/SnMe_4$ system.

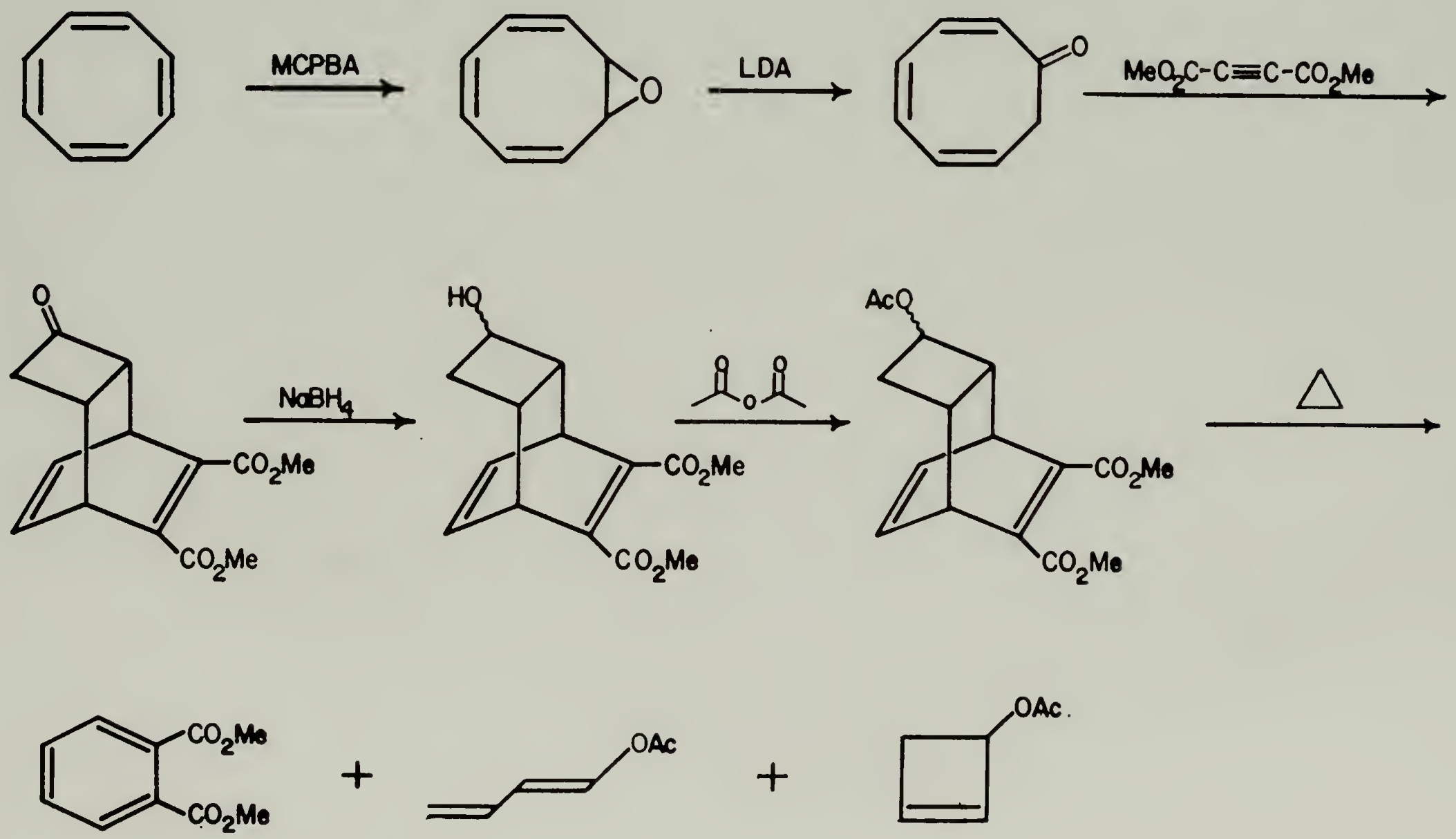
Copolymerization of DCCB and NBE with the $WCl_6/SnMe_4$ Catalyst System

Copolymerizations were run with the $WCl_6/SnMe_4$ system (IV-25, 27, 31, 33) using the two types of copolymerizations listed in the catalyst section. After some trial copolymerizations with NBE and *cis*-2-hexene to make sure that the products were going to stay in solution, we ran both types of copolymerizations with DCCB/NBE at room

temperature and at 0°C. At each temperature, we added a composite mixture of DCCB, NBE, *cis*-2-hexene and nonane as the internal standard to Tube A. To the other tube (B), we added the DCCB solution first, followed by a composite solution of NBE, *cis*-2-hexene and nonane 20 min later. The reference ratio of DCCB to nonane for the Tube B was the same as that for Tube A. In the room temperature reaction, there was a third tube that we added NBE to after a 20 minute delay, but it did not contain any chain transfer agent and became too thick to sample almost immediately. Attempts to redissolve the gel by dilution with chlorobenzene were unsuccessful. The ratio of $WCl_6/SnMe_4$ for these reactions was 1/1.4 instead of 1/2 due to an oversight. These reactions were monitored using both the AN600 and DC200 GC columns. The actual ratios of the areas were slightly different on each column for a given reaction mixture, but the relative differences in the amounts of DCCB should have been equivalent.

Metathesis Studies with 3-Acetoxycyclobutene

We first prepared ACB on a small scale, in order to carry out a few preliminary metathesis experiments. These trial polymerizations were promising enough that we synthesized ACB was on a larger scale and then looked at the metathesis behavior with the $WCl_6/SnMe_4$ system in greater detail. ACB was synthesized according to the procedures established by Cope[12-13] and Wiberg[14], as shown in Scheme 2.4. Gantler[15-17] had reported a more efficient route to cyclooctatrieneone, but we could not reproduce his results and abandoned this approach in favor of the Wiberg procedure.



Scheme 2.4. Synthesis of 3-Acetoxycyclobutene.

Monomer Preparation for Preliminary Metathesis Experiments

Fractions III-81 B and C from the spinning band distillation of the pyrolysis reaction were combined and dried over CaH_2 without further purification in the preliminary metathesis experiments. The percentage of ACB in these sample (as determined by GC) was multiplied by the sample weight to give the amount of ACB present. This quantity was used to calculate the concentration of the solutions used for metathesis. A total of 7 mL of dry chlorobenzene were used to wash fractions B and C into a graduated storage tube which contained 3Å molecular sieves. The sieves had been activated by heating at 350°C for 36 h under a steady flow of nitrogen. The solution was distilled away from the sieves after two freeze-pump-thaw cycles, and 0.15 mL of dry nonane were added as an internal standard. The final solution was 0.13 M in ACB and 0.10 M in nonane. The major impurity in this solution was 1-acetoxybutadiene (0.03 M).

Preliminary Metathesis Polymerizations of 3-Acetoxycyclobutene with $WCl_6/SnMe_4$

Details of the conditions for these polymerizations are shown in Table 2.2. (III-87, 88, 89, 91, 92) Reactions were monitored by GC using an AN-600 column at 100°C. Retention times (min): ACB 3.98, chlorobenzene 9.65, nonane 8.03(int. std).

These preliminary reactions showed that ACB was consumed in the presence of $WCl_6/SnMe_4$, but they were not carried out on a large enough scale to characterize the products. The concentration of ACB in these reaction mixtures was too low to obtain consistent GC data, possibly due to leakage at the o-ring seals in these reaction tubes. These initial studies did show however that ACB was consumed in the presence of $WCl_6/SnMe_4$, and that the polymerization of NBE was slower when ACB was present. With this in mind, ACB was synthesized on a larger scale and further metathesis studies with the new material are reported below. Details of the monomer purification are also included because the impurities present affect the metathesis behavior of ACB.

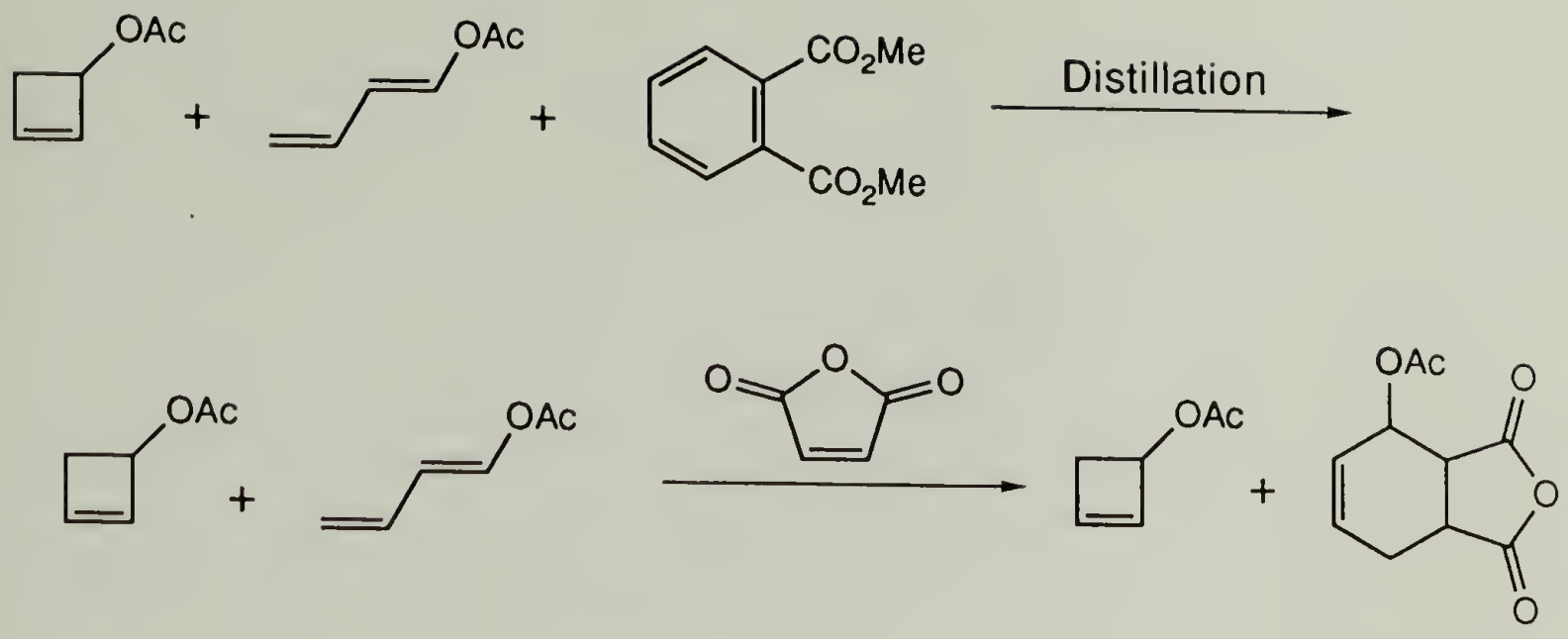
Table 2.2. Polymerization of 3-Acetoxycyclobutene with $WCl_6/SnMe_4$.

Reaction	W : Sn : Monomer	Temp °C	Method	Comonomer	Monomer Consumed after 24h
III-87	1 : 2 : 27	18	A*	None	0%
III-88	1 : 2 : 13	50	A*	None	15% ACB
III-89	1 : 2 : 13	50	A*	NBE	24% ACB 65% NBE
III-91	1 : 2 : 13	50	A*	NBE	49% ACB 20% NBE
III-92-1	1 : 2 : 13	50	B**	None	40% ACB
III-92-2	1 : 2 : 13	50	B**	NBE	58% ACB 86% NBE

* Monomer added after 20 minute aging period.
** $SnMe_4$ added last

Purification of 3-Acetoxycyclobutene

ACB was chemically separated from 1-acetoxybutadiene by reacting the latter with maleic anhydride as shown in Scheme 2.5. This was repeated a second time because a significant amount of the butadiene remained after the first treatment. On a small scale, the crystalline Diels-Alder adduct was separated from the rest of the reaction mixture by trap-to-trap distillation to yield a mixture of 12% maleic anhydride and ACB. The Wiberg procedure called for filtering out the adduct, taking the mother liquor up in pentane, drying it over Na_2SO_4 and then a final distillation to obtain pure ACB, but this was not practical on the 0.5 g scale.



Scheme 2.5. Purification of 3-Acetoxycyclobutene.

After removing the ring-opened acetoxybutadiene, the ACB was still contaminated with 5-10% maleic anhydride. To isolate the ACB, the sample was diluted with 10 mL of chlorobenzene and heptane (metathesis reaction solvent and internal standard, respectively) and the mixture was distilled on a spinning-band column, leaving the maleic anhydride in the pot. The boiling points of the pertinent components are shown in Table 2.3. Although some of the first fractions contained low boiling impurities, no maleic anhydride contamination was seen when the fractions were evaluated by NMR, GC.

Table 2.3. Boiling Points of ACB Product Mixture Components.

Component	Boiling Point °C
3-acetoxycyclobutene	140
chlorobenzene	132
maleic anhydride	200
nonane	151

Monomer Preparation for Metathesis Experiments

Fractions from the spinning band distillation were combined with chlorobenzene and nonane to form solutions of the appropriate molarity for metathesis studies with $WCl_6/SnMe_4$. Each solution (IV-69A, B, C) was dried over CaH_2 in the refrigerator, distilled trap-to-trap after a minimum of two freeze-pump-thaw cycles, and transferred via cannula into a graduated storage tube. This was stored in the freezer in a Ball jar and redistilled in the same manner several times during the course of the experiments.

Metathesis Experiments.

Metathesis reactions (III-71, 73, 75, 79, 85) with norbornene (NBE) or 1,5-cyclooctadiene (1,5-COD) were run as control reactions before each set of the ACB reactions to verify the health of the catalyst. Reaction conditions are listed in Table 2.4. Polymerizations were run in 28 mm diameter tubes with greased ground glass joints and 4 mm teflon stopcocks. Tubes were flushed with a copious amount of nitrogen before

Table 2.4. Polymerization of ACB with $WCl_6/SnMe_4$.

Reaction	Molarity in ACB		Volume of Monomer added	% Monomer Consumed	Moles ACB consumed per mole WCl_6
(Ntbk IV)	Monomer Solution	Reaction Mixture			
IV-71	0.6*M*	0.3*M*	0.30 mL	15.4	5.2
IV-73	0.6*M*	0.3*M*	0.30 mL	21.7	7.5
IV-75	0.6*M*	0.3*M*	0.30 mL	NR	NR
IV-79	1.1*M*	0.5*M*	0.20 mL	4.2	1.7
IV-85A	1.1*M*	0.6*M*	0.25 mL	2.3	1.2
IV-85B	1.1*M*	0.5*M*	0.15 mL	16.8	5.4

being charged via syringe with 0.1 mL each of 0.05 M WCl_6 and 0.10 M $SnMe_4$ (both catalyst components in chlorobenzene). Addition of $SnMe_4$ was the t=0 point and the catalyst was aged an average of 20 min before 0.3 mL of monomer solution was added via syringe. The monomer solutions contained nonane as an internal GC standard. Reactions were monitored sparingly by GC to avoid possible contamination during sampling. Small aliquots were removed under positive nitrogen pressure via cannula. Reactions were run at room temperature, and the ratio of ACB to WCl_6 was 30/1-35/1.

Post Reaction Analysis

After GC analysis, the low molecular weight components of the reaction mixture were separated under nitrogen from the rest of the reaction mixture (including catalyst residues) by two freeze-pump-thaw-cycles and trap-to-trap distillation at 1.0 mm. Benzene-d_6 was added to the residues that remained in the pot to extract any soluble products for NMR analysis. The reaction tubes were tared before the reactions for IV-77 and IV-85 to find out the weight of the solid residue. Using 300 MHz NMR, each of the components (the composite reaction mixture, mother liquor, soluble residues) was examined for evidence of metathesis products and monomer decomposition.

Metathesis Studies with 1,3-Cyclooctadiene

Monomer preparation

1,3-COD was used as received from Aldrich, without further purification except for distillation from CaH_2. Monomer solutions of 1,3-COD (5.4 M) were made up using decane as both the internal standard and the solvent. These solutions were dried over CaH_2, distilled trap-to-trap after three freeze-pump-thaw cycles and cannulated into graduated storage tubes. Solutions of norbornene (NBE, 1.2 M) were prepared by

dissolving the appropriate amount of NBE in chlorobenzene and distilling the composite solution under vacuum, using a standard still head. Monomer solutions containing both 3.0 M 1,5-COD and 3.0 M 1,3-COD were made up in decane and distilled trap-to-trap as described above for the homopolymerization experiments.

Metathesis Experiments

Reaction tubes with 24/40 or 28/34 ground glass joints were preferable to those with #25 o-ring joints connecting tube tops and bottoms because the o-ring seals could be swollen by the reaction components at elevated temperatures, possibly changing the quantitative relationship between the monomer and internal standard. Round bottomed flasks with septa were also used for short term (< 1hr) reactions, such as the control reactions with 1,5-COD or the qualitative test reactions with 1,3-COD. Some reactions were run at 75°C to increase product solubility, because if significant amounts of cyclohexene were eliminated from each poly(1,3-COD) chain, then the resultant polymer would be less soluble due to the increased conjugation along the chain. Initial monomer/catalyst ratios of between 100/1 and 50/1 were selected to avoid the non-metathesis side reactions possible at high concentrations of catalyst.

The relative concentrations of reaction components was monitored by GC. The monomer solutions were diluted with chlorobenzene and used as reference standards for the polymerizations. The initial ratio of 1,3-COD to decane for each reaction was an average of 3-5 GC runs of the reference standard solution. No zero point reference was used for NBE or cyclohexene, because NBE was added later to a reaction mixture which already contained the internal standard, and cyclohexene was not present as a starting material.

GC Conditions: OV-101@ 90°C for 6.5min, increasing at 25°C per minute to 130°C. Retention Times (min): Cyclohexene (1.6), NBE (2.0), chlorobenzene (4.1), 1,3-COD (5.6), 1,5-COD (6.8), *n*-decane (8.6).

Homopolymerizations

The main objective of these reactions was to produce as much cyclohexene as possible from the interaction of poly 1,3-COD with $WCl_6/SnMe_4$. (IV-39, 41, 44, 51, 55, 57, 65, 83) To this end, reactions were run for long periods of time, and additional aliquots of catalyst were added to some reactions when monomer consumption and cyclohexene production leveled off. Most reactions were run using Method A where the tungsten and tin catalyst components were mixed and then allowed to age 5-20 min before adding the monomers.

Copolymerization Type I

(IV 47, 47, 49, 53) A comonomer (NBE) which forms a highly reactive carbene was added to a polymerization in progress to see if it could speed up the rate consumption of 1,3-cyclooctadiene. A solution of 1,3-COD in decane (1.0 mL/5.4 M) was added to the catalyst mixture. After 5-20 min, a solution of NBE in chlorobenzene (2.0 mL/1.2 M) was added. Table 2.5 outlines the experimental details.

Copolymerization Type II

(IV 58, 59, 61) Equal amounts of 1,3-COD and 1,5-COD were added to the catalyst mixture at the same time. If the polymer of 1,3-COD was tying up the catalyst, then perhaps two comonomers would form a random copolymer which would be more amenable to the formation of cyclic oligomers. Copolymerizations with 1,5-COD are shown in Table 2.6.

Table 2.5. Copolymerization of 1,3-COD and NBE: Type I

Ntbk. Ref.	Ratio of 1,3-COD/NBE	Ratio of 1,3-COD/WCl_6	Gelation Time	Temperature ℃	Maximum % of 1,3-COD
IV-47-1	2.2 / 1	72 : 1	2 Hrs	75	26.8
IV-47-2	2.2 / 1	72 : 1	2 Hrs	75	9.9
IV-49-1	3.1 / 1	72 : 1	6 Hrs	75	33.4
IV-49-2	3.1 / 1	72 : 1	6 Hrs	75	31.3

Table 2.6. Copolymerization of 1,3-COD and 1,5-COD: Type II

Ntbk. Ref.	1,3-COD/1,5-COD	1,3-COD/WCl_6	Temperature ℃	Reaction Time	%1,3-COD consumed	CXE/DEC
IV-61-1	1 / 1	30 :1	75	129 Hrs	52.3	.0031
IV-61-2	1 / 1	30 :1	75	129 Hrs	52.6	.0035
IV-63-1	1 / 1	30 :1	22	114 Hrs	21.7	.0018
IV-63-2	1 / 1	30 :1	22	114 Hrs	24.9	.0023

Calculation of the Moles of Cyclohexene Produced per Mole of 1,3-COD Consumed

The response factors for 1,3-COD and cyclohexene were determined by injecting known mixtures of the two onto the GC. (IV-57, 86) Although more data points would be necessary to determine the response factors accurately, this crude measure did show that the actual amounts were at least within the same order of magnitude as those seen on the GC. Because there was several orders of magnitude difference in the amounts of cyclohexene produced and those expected for the amounts of 1,3-COD consumed in the polymerizations, the calculations described below were carried out without correcting for the difference in response factors. A strict determination of the response factors would not have changed our qualitative conclusions concerning the relative differences between the polymerizations in these studies. The equations shown in Scheme 2.6 below were used to calculate the number of moles of cyclohexene produced per mole of 1,3-COD consumed in a metathesis homopolymerization of 1,3-COD.

$$\frac{\dfrac{\text{Area of 1,3-COD Peak}}{\text{Area of Decane Peak}}}{\text{Reference Ratio of 1,3-COD/Decane}} = \%\ \text{1,3-COD Unreacted}$$

$$\%\ \text{1,3-COD Unreacted} \times (\text{Original \# of Moles}) = \text{\# of Moles of 1,3-COD Unreacted}$$

$$\frac{\text{\# of Moles of 1,3-COD Unreacted}}{\text{Area of 1,3-COD GC Peak}} = \frac{\text{x moles CXE}}{\text{Area of CXE GC Peak}}$$

$$x = \text{\# of Moles of CXE Produced}$$

$$\text{\# of Moles 1,3-COD Consumed} = (\text{Original \# of Moles}) - (\text{\# of Moles Unreacted})$$

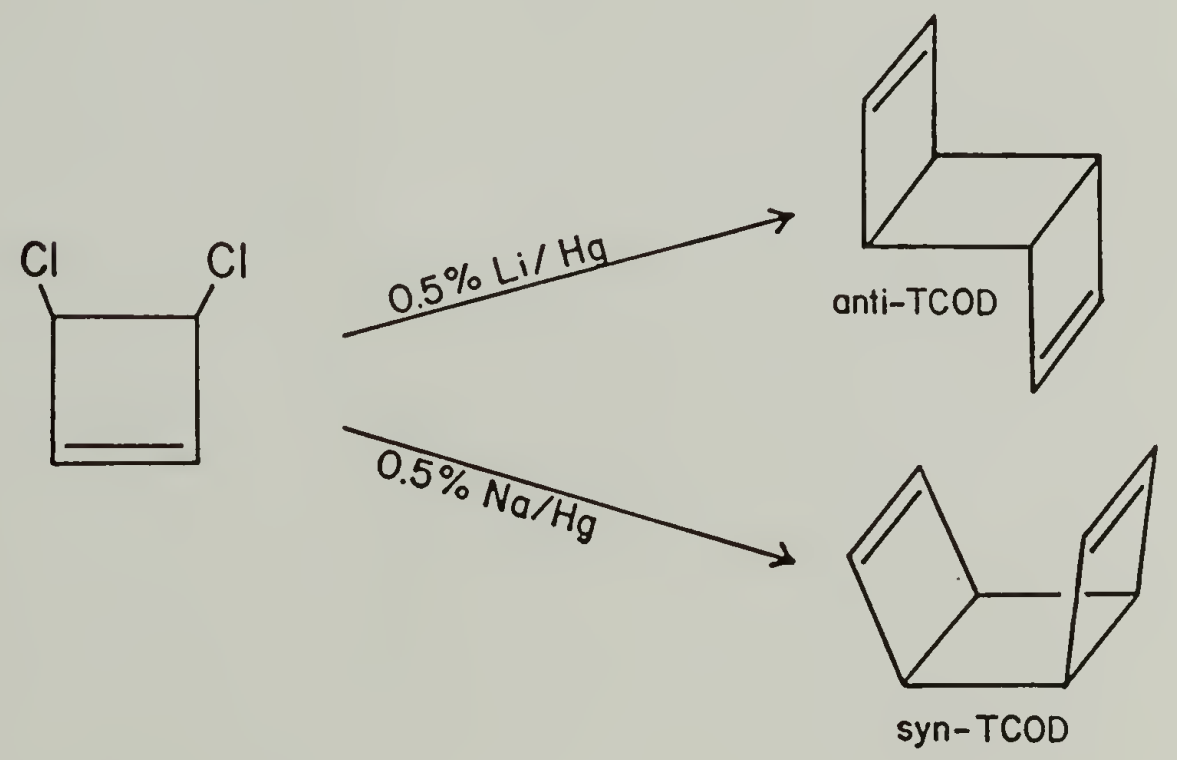
$$\frac{\text{\# of Moles of CXE Produced}}{\text{\# of Moles of 1,3-COD Consumed}} \leq\leq 1$$

Scheme 2.6 Calculation of the Moles of Cyclohexene produced per Mole of 1,3-COD Consumed.

syn-Tricyclo[4.2.0.0^{2,5}]octa-3,7-diene (TCOD)

Monomer Preparation

The synthesis of *syn*- and *anti*-tricyclo[4.2.0.0^{2,5}]octa-3,7-diene is shown in Scheme 2.7, as reported by Avram[18] and Paquette.[19] The synthesis and purification of TCOD are summarized below, along with the major modifications used to optimize the literature procedures. Details of the synthesis are described in detail in the Appendix.



Scheme 2.7. Synthesis of *syn*- and anti-tricyclo[4.2.0.0^{2,5}]octa-3,7-diene.

TCOD was synthesized in 30% yield from 3,4-dichlorocyclobutene, using the procedures described by Avram, with the addition of HMPA to the reaction mixture, as suggested by Paquette. A small amount was purified as the silver salt to yield 0.5 g of a clear colorless oil for GC calibration and characterization purposes. The remainder was

diluted with a mixture of heptane and chlorobenzene to optimize the total yield of TCOD. These diluents were chosen for their applicability to the olefin metathesis reactions as an internal standard and reaction solvent, respectively. Their function was to isolate the TCOD from impurities which boiled either higher or lower. The mixture was distilled on a 36" Perkin Elmer Model 246 teflon spinning band column. GC analysis of the distillation fractions indicated that a total of 3.1 g of TCOD were present in solution with various amounts of heptane and chlorobenzene.

Summary of Procedure Modifications. Several small scale reactions were run both with and without Paquette's suggested addition of HMPA as a cosolvent. ^{1}H-NMR spectra of the crude reaction products and of the trap-to-trap distillation product indicated that the syn isomer of TCOD was formed in approximately 50% yield. Key issues in the reaction procedure were the agitation of the reagents to affect complete mixing, and the separation of reaction products. After investigating the use of a glass mechanical stirring paddle, sonication in conjunction with water jacket cooling of the reaction flask and the addition of glass beads to the mechanically stirred mixture, the latter method was chosen as the most effective. Variations on the workup conditions for the organic reaction products included distillation on a small pig still, crude separation of the lower boiling products via trap-to-trap distillation to avoid decomposition of *syn*-TCOD and removal of the ether via rotovap followed by extraction of the HMPA with water. The latter method was best with respect to yield and convenience. Details of the final synthesis procedure and the separation of DCCB and *syn*-TCOD are given in the Appendix.

Purification of of *syn*-TCOD by Spinning Band Distillation. In order to optimize the total yield of TCOD, the product mixtures from V-55 and V-59 were diluted with chlorobenzene and heptane and then distilled on a spinning band column to separate TCOD from DCCB and any other impurities present (V-65). The low boiling impurities distill over before the heptane, and the chlorobenzene prevents the higher boiling

impurities from coming over with the TCOD. See Table 2.7. Heptane was suitable as an internal standard for TCOD given the GC columns available, and chlorobenzene was a common solvent for these reactions.

Table 2.7. Boiling Point Schedule for Purification of TCOD via Spinning Band Distillation.

Compound	bp°C/ 40 mm	bp°C/ 760 mm
Ethyl Ether	<0	35
Pentane	<0	35
Heptane	20	95
a-TCOD	40	120
s-TCOD	45	125
Chlorobenzene	48	132
Dichlorobutadiene	55	140
Cyclooctatetraene	60	142
DCCB	70	160
HMPA	135	235

An Analabs Superpak II column (70°C) was used to analyze fractions from the spinning band distillation of TCOD. GC analysis of the fractions from the spinning band distillation showed that *syn*-TCOD was synthesized in 30% yield to give 3.1 g of a colorless oil which was mixed with heptane and chlorobenzene in varying proportions. Combined fractions of *syn*-TCOD from this distillation were used in the metathesis experiments described below.

Purification of a Small Amount via the Silver Salt for GC Calibration and General Characterization. A small amount of TCOD was needed for GC calibration and NMR/IR (V-61). 1.6 g of the product of V-55 was shaken in 5 mL of a saturated $AgNO_3/H_2O$ solution. This was then shaken for 10 min with 15 mL of saturated NaCl solution to liberate TCOD, which was distilled trap-to-trap to yield a clear colorless oil.

Olefin Metathesis Reactions with TCOD

Metathesis Polymerizations of TCOD in solution with $WCl_6/SnMe_4$

Polymerizations were carried out in tubes which were sealed with teflon stopcocks and 28/34 ground glass joints. Catalyst and monomer solutions were prepared with freshly distilled chlorobenzene as the solvent. $WCl_6/SnMe_4$ catalyst solutions were tested by running COE homopolymerizations either at the same time or directly before the polymerization reactions involving TCOD.

Homopolymerization. 0.25 mL of 0.02 M WCl_6 solution and 0.17 mL of 0.12 M $SnMe_4$ were added to a reaction tube which had been purged with nitrogen. The red-brown colored catalyst solution was allowed to age 10 min before adding 1.00 mL of 1.0 M TCOD solution which contained heptane as an internal GC standard. The reaction mixture solidified instantly upon the addition of monomer to yield a granular solid. A solid state NMR of this sample after one month showed only several species of carbon bonded to oxygen were present, indicating extensive oxidation.

Copolymerization with Cyclooctene (1). A mixture of TCOD and COE were copolymerized by adding the catalyst to a mixture of both monomers. $SnMe_4$ (0.50 mL, 0.04 M) was added to each of two reaction tubes which had been charged with 2.00 mL of a 1.0 M COE solution that included nonane as an internal standard. One of the tubes was charged with 0.10 mL of a solution which was 1.0 M in both heptane and TCOD. A reference sample for GC was taken before adding 0.50 mL of 0.02 M WCl_6 to each of the tubes at t=0. The disappearance of monomer was followed by GC. The combined products from three polymerizations to which TCOD had been added were precipitated via

cannula into methanol, filtered and dried under vacuum (0.07 mm) overnight. The rubbery polymer was sliced into small pieces, placed in an NMR tube and swollen with $CDCl_3$.

Copolymerization with Cyclooctene (II). TCOD was added to a COE homopolymerization in progress. 1.50 mL each of 0.02 M WCl_6 and 0.04 M $SnMe_4$ were added to a nitrogen-purged reaction tube and stirred. After 15 min, 6.00 mL of 1.0 M COE was added. A GC sample taken 20 min. after monomer addition showed that 47% of the COE had been consumed. At this point, 0.030 mL of a solution which was 0.5 M in both TCOD and heptane was introduced and the reaction mixture stirred until it gelled. Some of the product was removed from the flask and swollen in chlorobenzene. After vigorous stirring, the liquid part was tested by GC for residual monomer. Another portion was dried on the vacuum line at (.07 mm) overnight and the resulting rubbery polymer was sliced up, placed in an NMR tube and swollen with $CDCl_3$. As a control reaction, poly(COE) was prepared in the same manner, except no TCOD was added. A nitrogen-purged reaction tube was charged with 0.50 mL each of 0.02 M WCl_6 and 0.04 M $SnMe_4$. After 15 min, 2.00 mL of a 1.0 M COE solution which contained nonane as an internal standard was added to the reddish-brown catalyst mixture. The product from this reaction was also prepared for ^{1}H-NMR and ^{13}C-NMR analysis, as described above for the TCOD sample.

GPC Analysis of a Crosslinking Experiment using Shorter Polymer Segments

A chain transfer agent (*cis*-2-hexene) was incorporated into these experiments to keep the reaction solutions from becoming too viscous. GPC analysis was used to examine effects of TCOD as a crosslinking agent on the distribution of molecular weights in the reaction mixture at equilibrium (VI-8-11).

Conditions: Room temperature

Monomer/WCl_6/$SnMe_4$ = 200/1/2

Monomer/*syn*-TCOD = 120/1

Monomer/*cis*-2-hexene = 30/1

Both monomer and TCOD solutions were diluted to half of their original molarity to prevent gelation of the products. WCl_6 (0.9 mL of 0.002 M) and $SnMe_4$ (0.9 mL of 0.004 M) were combined in each of two reaction tubes. After aging 15-min, 7.25 mL of 0.5M COE solution (which also contained 7.0 mmoles of heptane and 0.23 mmoles of *cis*-2-hexene) was introduced to each. After one hour, ~50% of the COE had been consumed, according to GC results. One half of the reaction mixture (4.5 mL) in tube A was removed via syringe for GPC analysis, and 0.060 mL of 0.25M TCOD were added. After 3.75 h, the reaction mixtures in both tubes were precipitated into methanol and the solvent removed via rotovap, followed by trap-to-trap distillation.

All of the TCOD had been consumed by the time the first GC point was taken, although the internal standard peak (heptane) was clearly present. The products were visibly inhomogeneous after the workup. There were small clumps of gray solid as well as low molecular weight oils and small beads that looked like water. GPC of these materials proved difficult, possibly due to water contamination of the samples. Typical concentrations for GPC are 1-3 mg/mL. Even at 80 mg/mL, there was barely enough signal to collect data. GPC traces using a refractive index detector are shown in Figure 2.4. If we look only at retention times and interpolate from the polystyrene calibration curve, the molecular weight clearly increased from the undisturbed control sample to the crosslinked sample. These experiments did not account for how the GPC handles branched species or for the fact that the polymerizations may not reach equilibrium before the catalyst dies. Given the ambiguities introduced by the detection of branched

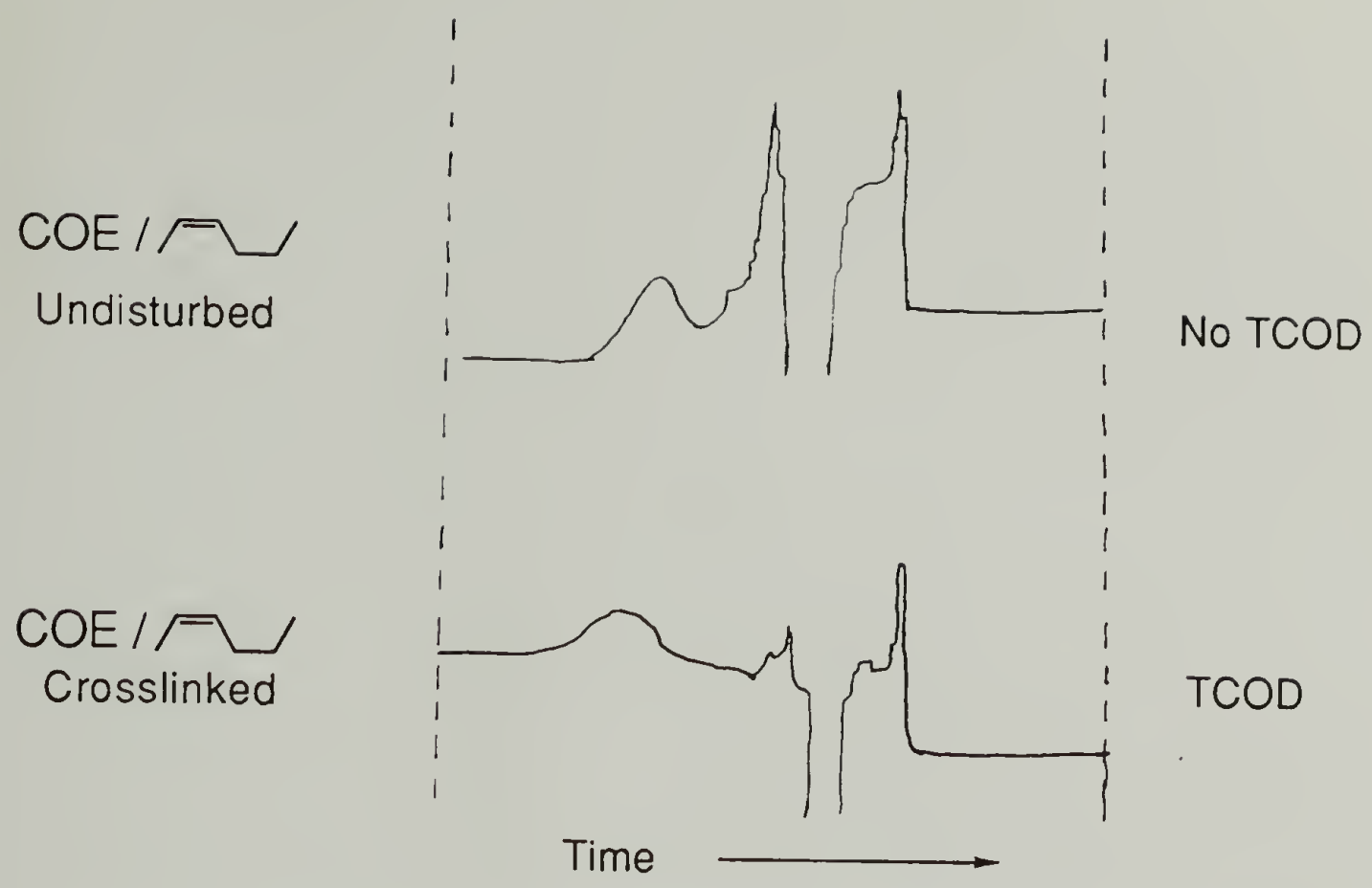


Figure 2.4. GPC Traces of a COE Copolymerization with *cis*-2-hexene as a Chain Transfer Agent a) No crosslinking agent. b) TCOD added.

species in the GPC and the mixture of products obtained in these reactions, swelling and modulus measurements seemed more appropriate to measure the differences between networks with different crosslinking agent concentrations.

Synthesis of Solid Crosslinked Samples using (WCl_6/Et_2AlCl)

Because these network samples were designed to be crosslinked and therefore insoluble, we needed a catalyst which would synthesize materials in a form suitable for testing. A high monomer to catalyst ratio was also required, so that only small amounts of catalyst would be present to obscure the changes in physical properties due to the different crosslink densities. The Metton™ catalyst system (WCl_6/Et_2AlCl) satisfied all of these

criteria. Hercules uses this two part catalyst system to polymerize dicyclopentadiene in a Reaction Injection Molding (RIM) process to produce a high modulus thermoset material with exceptional impact strength. Macosko et. al.[9] published the procedure for polymerization of dicyclopentadiene (DCP) and norbornene (NBE). Catalyst preparation was described previously in this chapter.

Determining Optimal Configuration and Composition for Network Samples. (VI-15) Homopolymers of NBE with the Metton™ system were difficult to prepare because the Et_2AlCl solution of NBE had to be heated as it was transferred to prevent solidification of the NBE. In the initial attempts, the NBE foamed when the 2 components reacted, even when the samples were cooled immediately after combination in a -30°C bath and a positive nitrogen pressure (~6 lbs) was maintained during the cure. The final products contained many voids, several millimeters in diameter and were not suitable for testing.

Macosko reported cure temperatures of 150-180°C with this system, making it reasonable to assume that the foaming problems with NBE (bp 96°C) were due to boiling of the monomer during the polymerization. DCP could be polymerized at these concentrations with WCl_6/Et_2AlCl because it boils at 170°C. The next logical step was higher boiling monomers which might produce rubber-like materials suitable for these studies. Neither COE (bp 145°C) or *cis*-cyclodecene (CDE, bp 232°C) produced homopolymers using these catalysts. A report by Dall'Asta[20] indicated that initiation below room temperature was required before letting the reaction warm up so that the polymerization could proceed, but these modifications were not effective. The reaction mixtures became slightly viscous over time, but precipitation into methanol gave only an oil did not indicate high polymer.

Copolymerizations of COE and CDE with NBE were both successful. The WCl_6 component was made up in CDE or COE and the Et_2AlCl component in NBE or vice-

versa, and the two were mixed. The most rapid and complete polymerizations resulted when a solution of Et_2AlCl/NBE was combined with a solution of the WCl_6 component dissolved in either COE or CDE. COE was chosen as the best comonomer over CDE because it gave more consistent results, and because the lower number of consecutive methylene units in the product networks would reduce the possible complication of apparent crosslinks due to crystallites.

Because this reaction was relatively fast and the catalyst was not reported to be as sensitive as some of the more traditional metathesis catalysts, several samples were prepared as thick films in teflon pans and as plugs in 10 mL beakers. Both of these shapes cured at different rates across the sample and some foaming was observed. The final product in the case of the films was a tough rubber at one end of the sample and a viscous liquid at the other. The best method for preparing consistent samples from the same batch of monomer was to combine the two catalyst components in 6 mL culture tubes (12 x 75 mm) which had been capped with rubber septa and flushed with nitrogen. The resulting samples were cylinders about 4 cm in length and 8 mm in diameter and reasonably homogeneous except for small voids (<1-mm) caused by bubbles.

Trial Networks. Before synthesizing an extensive series of networks, two trial networks of 100 and 400 monomer units between crosslinks, respectively were prepared to establish procedures for the different characterization methods (VI-53, 55). TCOD (0.125 mL of 1.0M and 0.25M respectively), was added to a total of 0.025 moles of an equimolar mixture of NBE and COE to give monomer/TCOD mixtures in the ratio of 200/1 and 800/1, respectively. These were divided into equal portions to make up the Et_2AlCl and WCl_6 components of the system. For each of the concentrations of TCOD, 1.0 mL each of the two catalyst components was transferred via cannula into 6 mL culture tubes capped with septa. The cure for this set of samples was not homogeneous. There were voids at the tops of the tubes and unpolymerized monomer at the bottoms. The solid

rubber portions in between were cut away and used for testing. The results of these initial tests were contradictory for both swelling and modulus, possibly due to an error in the amount of TCOD added to the samples or to a drastic dramatic difference in the degree of polymerization for the two sets of samples. However, they did enable us to optimize the procedures for physical characterization of these types of samples, as described in the following two sections.

Preliminary Swelling Measurements. The preliminary swelling tests were set up to look at the difference between methylene chloride and toluene as swelling solvents and to examine the effect of sample shape (rectangular chunks and thin disks) on the degree of swelling. Samples were cut with a fresh single-edged razor blade into disks (8 mm in diameter, 1-2 mm thick) and chunks (4 mm cubes), placed in 5 dram vials and covered with several milliliters of solvent. The results after 14 h are listed in Table 2.8.

Table 2.8. Preliminary Swelling Test Results for Solid TCOD Networks.

Sample Form	Percent Weight Increase		Solvent
	400 units VI-53	100 units VI-55	
Chunks	78.9	90.0	Toluene
	78.3	35.0	"
	76.5	92.5	"
Thin Disks	64.1	98.4	"
	67.2	102.2	"
	64.8	104.5	"
Smooth Film	88.1	122.5	"
Chunks	80.6	77.1	$MeCl_2$
	75.6	79.7	"
	85.6	83.2	"

These results were counter-intuitive to what we would expect from two networks that differ in crosslink density by a factor of four, indicating that our samples had different crosslink densities than those predicted by the initial stoichiometries. The more highly crosslinked network should have swollen less than the the less crosslinked one. No attempt was made to interpret these puzzling results in light of the physical inhomogeneities clearly present in the both these sets of samples before they were cut up for swelling experiments. Subsequent swelling studies used toluene to minimize the weighing errors because it is less volatile than methylene chloride. The difference in the degree of swelling between the thin film sample and the other sample shapes indicated that the measurements should be made over a greater amount of time to insure equilibrium results.

Preliminary Modulus Measurements. Materials with different crosslink densities should produce materials with different equilibrium elastic moduli, when measured above the glass transition temperature. The density of crosslinks can be related to the elastic modulus by the equation shown below.

$$G_e = \frac{\rho R T}{M_c}$$

M_c = Av. Molecular Weight Between Crosslinks
R = R=8.314J/°K-Mol,
G_e = Elastic Modulus (Pa)
T = Temperature (413°K)
ρ = Polymer Density

The IMASS Dynastat instrument was used to measure the equilibrium modulus of these trial networks and some other samples which did not contain any TCOD, but sample preparation difficulties led to problems with both precision and accuracy. Thick cylinders with parallel faces were required, and it was difficult to cut the faces straight or smooth enough to obtain valid measurements, despite numerous attempts and the use of several types of cutting techniques and blades. The presence of small ridges or burrs made consistent measurements difficult because these types of anomalies directly affected the amount of surface area over which the load was distributed and they led to a wide range of values for a single sample. These samples were too brittle at low temperature to cut smoothly and too soft at room temperature to cut straight. Despite these difficulties, several samples were tested, using frequencies of 0.5 Hz and 1.0 Hz, over a 150°C temperature range. Using the values at room temperature as a guide, the modulus of the lightly crosslinked sample was higher (9 MPa) than that of the more highly crosslinked one (4 MPa). These results were also contrary to our expectations, similar to the situation with the swelling tests. Repeated trials with these sample networks showed that the equilibrium modulus for a single network composition varied too much from sample to sample to evaluate the difference between the different compositions. When combined with the uncertainties associated with sample preparation, it was obvious that another method for measuring modulus differences between networks was required.

Sample preparation for the Polymer Labs Dynamic Mechanical Analysis (DMA) instrument was not as critical because it used thin (1 mm) cylindrical samples, and the parallax between the faces was not as critical. Bubbles and other irregularities present in these samples affect the modulus calculation for both the DMA and the Dynastat. However, some trial runs with the DMA indicated that it would provide more consistent

results for the series of network samples whose preparation is described below, due to sample preparation considerations.

Network series synthesis. Our objective was to produce a series of solid samples suitable for mechanical testing, because samples with different proportions of TCOD should have difference molecular weights between crosslinks and as a results should display differences in physical properties. In order to minimize the effects of using two monomers as the backbone for these networks, we made up a monomer solution which had a 1:1 molar ratio of COE to NBE by weighing the amount of NBE and then adding the appropriate weight of COE. This composite solution was then dried over CaH_2 and distilled with a standard still head. Five samples of 1.00 mL were weighed to establish a density of 0.860 g/mL for the composite solution. The number of moles of monomer in a given volume was determined by using this density and an average of the molecular weights of COE and NBE. In order to keep the conditions for producing these networks as consistent as possible, components were mixed in the same order, needles and syringes were subjected to the same drying procedures between each set of samples and the samples were processed in a continuous series. The procedure detailed below was strictly followed for each network composition (A-E) except for the sample labeled XT which did not contain any TCOD:

A solution of TCOD (5.61 M) was used as the base solution for a series of dilutions to create a range of crosslinking solutions, as shown in Table 2.9. The molarity of the first solution was determined by GC using the internal standard method. These calculations and the GC data can be found in Notebook IV.

Table 2.9. Stoichiometry for the Synthesis of Network Sample A-E, XT using WCl_6/Et_2AlCl.

Net-work	Amt of TCOD Solution	Amt of chloro-benzene	Molarity of TCOD Solution	Millimoles TCOD added	Ratio of Monomer to TCOD	Units between crosslinks	M_c
A	0.25mL "A"	0 mL	5.60*M*	1.40	18	9	912
B	0.75mL "A	0.75mL	2.80*M*	0.07	36	18	1823
C	0.75mL "B"	0.75mL	1.12*M*	0.28	89	45	4558
D	0.87mL "C"	0.75mL	6.02*M*	0.15	166	83	8487
E	0.87mL "D"	0.75mL	3.23*M*	0.08	309	155	15804
XT*	—	—	—	—	—	—	—

* No Crosslinking Agent Added

For each network composition, the crosslinking solution (0.25 mL) was added to 3.00 mL of a composite solution of NBE/COE in a 14/20 round-bottomed flask which also contained a small amount of CaH_2. Previous experience with trap-to-trap distillation of similar reagents had shown that relative concentrations did not change over the course of the distillation, and that small amounts of material could be quantitatively distilled using this method. This solution was then distilled from CaH_2 and divided into two equal portions for combination with the WCl_6 and Et_2AlCl catalyst solutions, such that the ratio of monomer to crosslinking agent was constant throughout each sample. Two samples were made of each network composition. The first was made by injecting 0.75 mL of each catalyst solution into a 6 mL culture tubes, using 1 mL gas-tight syringes. The tubes were capped with rubber septa and had been previously flushed with nitrogen. The WCl_6 solution was added first, followed by the less dense Et_2AlCl solution. The latter was added to the bottom of the tube such that mixing was achieved during the addition. The second sample was made by transferring the remainder of the WCl_6 solution into the culture tube via cannula, followed by the remainder of the Et_2AlCl component. Care was taken to insure that the nitrogen did not bubble up through the samples when the second aliquot was added, creating bubbles and voids in the samples. A positive nitrogen pressure was maintained in the sample tubes during the mixing process, and the tubes were turned end-over-end after both streams had been added to insure adequate mixing. Despite these precautions, there were some obvious differences between the samples. Sample D had a visibly greater proportion of bubbles from foaming, and Sample C was injected with a 30 μL excess of Et_2AlCl by mistake.

The samples produced by this method were smooth, brown, rubber-like sausages with the consistency of the average pencil eraser. To remove them from the tube, a hammer was used to break the tubes around the samples, with little, if any, visible damage

to the specimens. These were stored in teflon-sealed glass vials prior to mechanical and swelling tests.

Swelling Measurements (VI-74,82,92,93) Three sets of swelling tests were carried out on this series of network compositions. Two of them compared samples from each of the compositions A-E, XT, and the third study looked at the swelling characteristics of different slices of a single composition. For the two studies that looked at the entire series (VI-74, 93), thin slices (1 mm) of networks A-E, XT were cut, measured and weighed before being placed in small vials and covered with toluene. For VI-93, 2.00 mL of toluene were added to each vial using a gas-tight syringe with an automatic stop. The third study (VI-82) looked at an entire sample of single stoichiometry, network B, chopped into 6 individual pieces. These were placed in individual vials and 1.50 mL toluene was added in the same manner as for VI-93. Two samples (Networks A and XT) were pumped under vacuum to remove any volatile components before exposure to the swelling solvent. These samples (VI-92) were referred to as the "dry" samples.

For all of these studies, the samples were allowed to equilibrate over three days, and some were reweighed after several days to see if they changed. They were measured with standard calipers and weighed. Due to time constraints, a single weight measurement was used to establish the original sample weight before swelling. Because the final weight varied due to solvent evaporation and the amount of residual solvent left on the sample, at least three measurements were used to determine the final, swollen weight. In VI-74, both sample diameter and sample thickness were measured for each sample. The diameters were measured by placing the samples between two glass slides, and the diameter determined without consciously applying enough pressure to affect the measured diameter. These measurements were difficult because inconsistencies in the samples and deviations from circular geometries caused measurements of the same sample to vary

considerably, especially in thickness. The complete set of raw weights and dimensions, plus the calculations can be found in Notebook VI.

GC Analysis of Swelling Effluent. The swelling effluent from VI-82,93 was characterized by GC to determine the relative amounts of low molecular weight materials left in each sample. For the series of network compositions, the relative quantities of COE and NBE from each sample would be indicative of the relative degree of polymerization between samples. To this end, the concentrations detected in the swelling effluent were normalized by the original weight of the sample. This is slightly misleading because the weight of the different components being measured is also included in the initial weight. Analysis of the effluent from VI-82 gives the variation in swelling characteristics within a single sample and an idea of the total amount of monomer extracted and the average degree of polymerization for that sample. The complete set of data and calculations can be found in Notebook VI.

A 1 mL syringe which had been sealed off at the tip by the glass shop was used to prepare the calibration solutions and to make up the solutions of swelling effluent with the internal standard. Toluene (1.00 mL) was delivered into the calibration syringe to determine the mark which corresponded to 1.00 mL. For example, 1.00 mL of solution came to the 0.96 mL mark on the specific syringe used for these measurements. In determining the concentration of each of the reaction components in the swelling effluent, the internal standard was weighed into the calibration syringe and the swelling effluent was used to bring the level up to the 0.96 mL mark. The amount of internal standard was entered into the GC calibration table and then a sample of the swelling solution plus the internal standard was injected onto the column. Calculations used to determine the relative concentrations of the different components are detailed in Notebook VI.

Modulus Measurements. For reasons discussed earlier, the Polymer Labs Dynamic Mechanical Analyzer (DMA) was used to look at the effect of different proportions of TCOD on the modulus in the rubbery plateau region for the series of network compositions. Small disks, about 1 mm in thickness and 8 mm in diameter were cut with a single-edged razor blade and mounted in the DMA with the flat side of the sample against the grips.

References

1. Costello, C. A. *Ph. D. Dissertation*, University of Massachusetts, Amherst, 1987.

2. Shriver, D. F. Manipulations of Air Sensitive Compounds. McGraw-Hill, New York, 1969.

3. Ivin, K. J. Olefin Metathesis. Academic Press, London, **1983**. Chapter 2.

4. Thoi, H. H.; Reddy, B. S. R.; Rooney, J. J. *J. Chem Soc., Faraday Trans. I* **1982**, *78*, 3307.

5. Norton, R. L. *Ph. D. Dissertation*, University of Massachusetts, Amherst, Massachusetts, 1989.

6 Masuda, T.; Hasegawa, K.; Higashimura, T. *Macromolecules* **1974**, *7*, 728.

7. Mol, J.C.; Woerlee, E. F. G. *Chem. Commun.* **1979**, 330.

8. Calderon N.; Ofstead E. A., Judy W. A., *J. Polym. Sci., A-1* **1967**, *5*, 2209.

9. Matejka, L.; Houtman, C.; Macosko, C. W. *J. Appl. Polym. Sci.* **1985**, *30*, 2787.

10. Pettit, R. *Org. Syn.*, **1970**, *50*, 36.

11. Ivin, K. J. Olefin Metathesis, Academic Press, London, **1983**. p. 241.

12. Cope, A.C.; Tiffany, B. D. *J. Am. Chem. Soc.* **1951**, *73*, 4158.

13. Cope, A.C.; Schaeren, S. F.; Trumbull, E. R. *J. Am. Chem. Soc.* **1954**, *76*, 1096.

14. Wiberg, K. B.; Williams, V.Z.; Fredrich, L.E. *J. Am. Chem. Soc.* **1970**, *92*, 564.

15. Ganter, C.; Pokras, S. M.; Roberts, J. D. *J. Am. Chem. Soc.* **1966**, *88*, 4235.

16. Gasteiger, J.; Gream, G. E.; Huisgen, R.; Konz, W. E.; Schnegg, U. *Chem Ber* **1971**, *104*, 2412.

17. Johnson, B. F. G.; Lewis, J.; Weger, D. J. Chem Dalton **1976**, *19*, 1874.

18. Avram, M.; Marica, E.; Dinulescu, I.; Farcasiu, M.; Elian, M.; Mateescu, G.; Nenitzescu C. D. *Chem. Ber.* **1964**, *97*, 383.

19. Paquette L. A.; Carmody M. J. *J. Amer. Chem Soc.* **1976**, *98*, 8175.

20. Dall'Asta, G.; Manetti, R. *Eur. Polym. J.* **1968**, *4*, 145.

CHAPTER 3

DISCUSSION

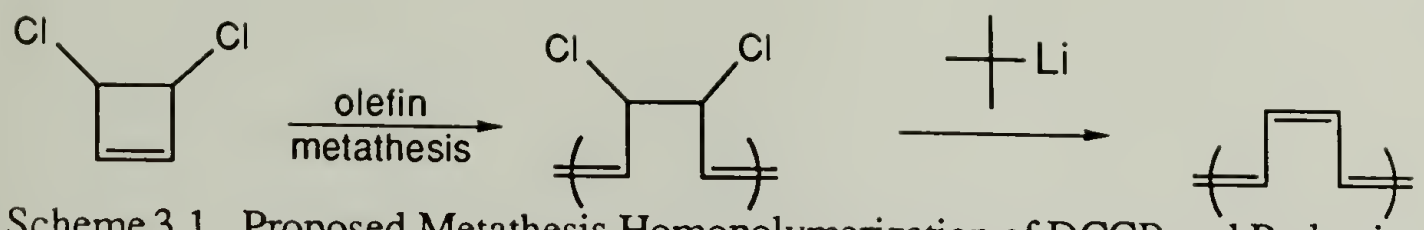
Metathesis Polymerization of Substituted Cyclobutenes

Our goal was to synthesize processable precursors of polyacetylene (PA) which could be converted in a controlled manner into electrically conducting polymers. At the same time, we wished to investigate unexplored applications of metathesis catalysts toward the polymerization of strained functional group containing monomers. In pursuit of alternate routes to polyacetylene, it made sense to exploit our ability to make polymers with double and triple bonds in the main chain. Conveniently, the metathesis polymerization of 3,4-substituted cyclobutenes should yield alternating copolymers of acetylene and substituted ethylenes. The ethylene character of these polymers should enhance solubility properties such that they can be processed into appropriate shapes and then be converted *in-situ* to PA.

Metathesis Polymerization of 3,4-Dichlorocyclobutene

Metathesis Homopolymerization Studies of DCCB

We chose DCCB as the first candidate monomer in these studies because it was synthetically accessible as well as commercially available, and because the transformation to PA from the parent metathesis polymer could be achieved by a variety of methods established in the literature.[1] The metathesis homopolymerization of DCCB and its reduction to PA are shown in Scheme 3.1.



Scheme 3.1. Proposed Metathesis Homopolymerization of DCCB and Reduction to PA.

Both homopolymerizations of DCCB and copolymerizations with norbornene were studied, using the homogeneous ($WCl_6/SnMe_4$) and heterogeneous ($Re_2O_7/SnMe_4/Al_2O_3$) metathesis catalyst systems.

Homopolymerization of DCCB with $WCl_6/SnMe_4$. We initially chose the $WCl_6/SnMe_4$ system because it was a homogeneous catalyst system which was compatible with functional groups, specifically chlorinated olefins.[2-4] A heterogeneous system would complicate product analysis if the metathesis products of DCCB were insoluble under reaction conditions. As shown in Table 3.1, DCCB was reacted under several sets of polymerization conditions, using the $WCl_6/SnMe_4$ catalyst system. Some of the reactions were run at 80°C to improve product solubility, based on reports by other groups who employed higher temperatures[5-7] when polymerizing functionalized olefins. Raising the temperature helped overcome the higher energy barriers to complexation of the polar monomers onto the "carbene-bearing" metallic site when polymerizing olefins with functional groups.[8]

In order to convert the maximum amount of DCCB to polymer, additional catalyst was injected, as noted in the table. GC sampling showed that the rate of disappearance of DCCB leveled off after each addition. The catalyst was a good red color in all reactions except III-29, where it changed to brown after 20 h. Reaction III-29 looks less than

Table 3.1. Metathesis of DCCB with $WCl_6/SnMe_4$.

Reaction	WCl_6:$SnMe_4$: Monomer	Temperature (°C)	Monomer Consumed	Total Reaction Time (h)
III-25	1 : 1.5 : 16	25	12%	24.0
			17%	28.0
			100%	44.0*
III-27	1 : 1.5 : 16	80	35%	9.5
			42%	11.0
			100%	18.0**
III-29	1 : 2.2 : 200	80	4%	7.0
			11%	19.0
III-31	1 : 2.2 : 200	80	2%	0.5

Note: * Additional catalyst added at 42.5 h.
** Additional catalyst added at 15.5 h.

successful at first, but a closer look at the sampling times shows that it was consistent with the other reactions up until the time that sampling was discontinued. In each of these experiments, a finely divided black solid fell out of solution almost immediately after adding the monomer to the catalyst solution. Although the powder-like nature of the precipitate made it difficult to visually correlate the amount of black solid produced with the disappearance of DCCB seen by GC, more black powder appeared each time fresh catalyst was added. Polymerization was distinctly slower than with non-functionalized cyclic olefins. For example, COE and 1,5-COD typically polymerize in less than 30 minutes at much lower concentrations of catalyst. Based on the limited number of experiments shown in Table 3.1, the monomer was consumed at a faster rate at higher temperatures and higher catalyst concentrations.

Elemental analysis of the finely divided black solid product is shown in Table 3.2 for reaction III-27. The powder oxidized in air and turned a yellow-brown color.

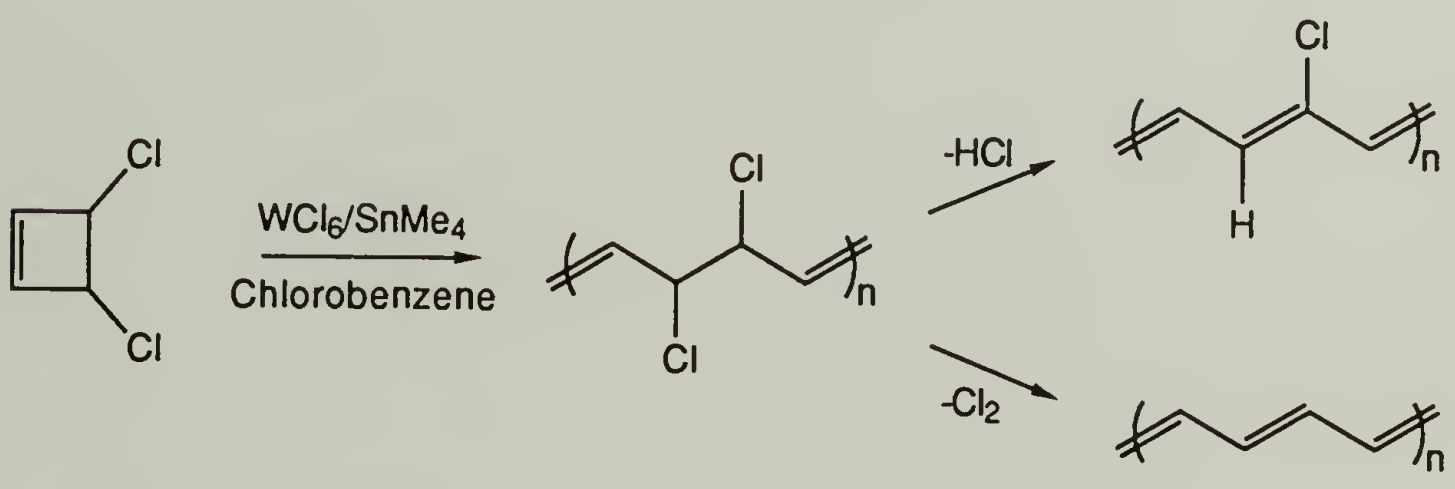
Oxidation of the powder and replacement of the chlorines by oxygen could account for some of the reduced chlorine content from that expected for poly(DCCB). The report from the analytical lab also indicated small amounts of cellulose fibers from the filter paper mixed with the black powder, which could have further contributed to discrepancies in the elemental analysis.

Table 3.2. Elemental Analysis for Poly(DCCB). (III-27)

Element	Found	Calculated
Carbon	39.0%	39.0%
Chlorine	10.2%	57.4%
Hydrogen	3.0%	3.3%

While this work was in progress, Brunthaler and Stelzer published a paper which described the metathesis of DCCB using the $WCl_6/SnMe_4$ catalyst system.[9] Their homopolymerization results indicated low yields of a black powdery reaction product which oxidized to a yellow-brown color in air and had a reduced chlorine content from the expected metathesis product. They did not specify their polymerization conditions, except to report that the ratio of $WCl_6/SnMe_4$ was 1/2, and that reactions were run in both chlorobenzene and dichloroethane, at -3°C and at 40°C. From UV, IR and elemental analysis results, they concluded that the polymerization product was a polymer with five or more conjugated double bonds. They identified their material as a polyacetylene-type polymer which displayed conductivities of $10^{-9}\ \Omega^{-1}\ cm^{-1}$ and $10^{-4}\ \Omega^{-1}\ cm^{-1}$, before and after doping with iodine, respectively.

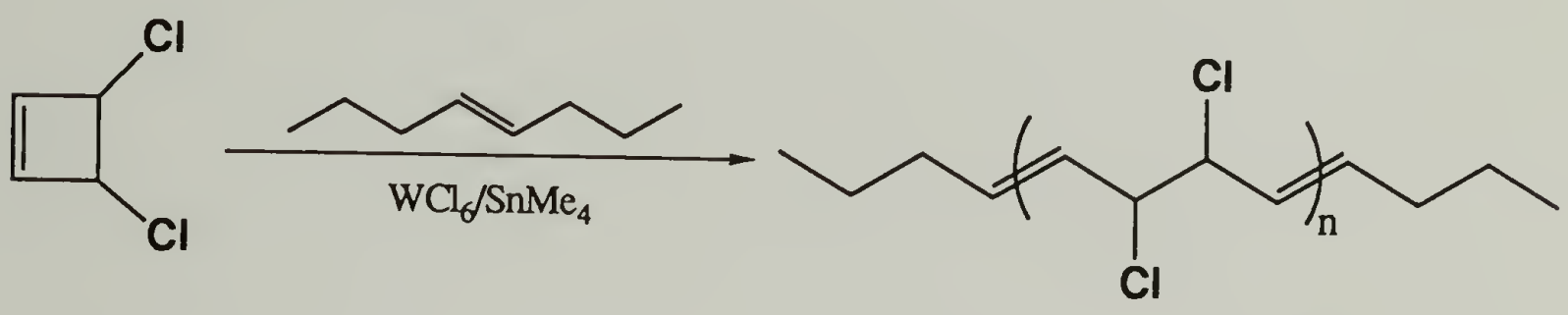
The reduced chlorine content of powder in both our results and those reported by Brunthaler indicates that some sort of elimination took place in the presence of the catalyst. Brunthaler proposed an in-situ elimination of either Cl_2 or HCl in the presence of $WCl_6/SnMe_4$, as shown in Scheme 3.2.[9] The upper mechanism was plausible because other WCl_6-based catalysts were reported to generate acidic species which led to cationic side reactions such as isomerization, alkylation and dimerization within the starting materials and products.[10,11] In fact, production of HCl has been reported for some WCl_6 catalyzed metathesis reactions.[12] Neither mechanism explains the magnitude of the discrepancy in the chlorine amounts seen by us, and we conclude that elimination of chlorine must be accompanied by oxidation of the resulting conjugated polymer. We would not expect high oxidative stability from highly unsaturated polymers containing carbon-chlorine linkages, and this sort of oxidation is likely if the final product of the metathesis reaction is a partially chlorinated form of PA. Because our products were similar in appearance to those described by Brunthaler, we did not pursue further characterization.



Scheme 3.2. Metathesis Homopolymerization of DCCB with $WCl_6/SnMe_4$. Side Reactions Reported by Brunthaler and Stelzer

Results of Brunthaler and Stelzer's cross-metathesis experiments between *trans*-4-octene and DCCB were encouraging because they indicated that ring-opened

products were formed with this system and that copolymerization was possible. As shown in Scheme 3.3, they obtained 6,7-dichloro-4,8-butadiene and 6-chloro-4,6,8-dodecatriene in low yield, as identified by GC-MS, along with small amounts of black powder and some low molecular weight materials containing more than one cyclobutene unit. Some of these samples had also lost chlorine, similar to the homopolymer situation. Clearly, metathesis products were formed with DCCB and the $WCl_6/SnMe_4$ system, but the elimination of chlorine to form a polymer with conjugated double bonds was not controlled under these conditions.



Scheme 3.3. Cross Metathesis between DCCB and *trans*-4-octene.

These polymerizations were slow compared to those with nonfunctionalized olefins. Brunthaler et al. claim that loss of HCl during polymerization gave a conjugated polymer which deactivated the catalyst. The catalyst may have been so tightly coordinated to the conjugated oligomers formed after the elimination of chlorine that fresh monomer was coordinated at a slower rate. In the case of pent-2-ene, metathesis is retarded by the presence of terminal olefins which coordinate strongly to the metal center.[13] DCCB might be incorporated more efficiently into the chain by adding another monomer which would form a different of type of carbene structure which was not inhibited by the presence of the conjugated units.

Alternatively, the rigid structure of the eliminated polymer may not have been soluble under reaction conditions and could have forced the propagating carbenes out of solution. We would expect the initial DCCB homopolymer to be soluble in chlorobenzene, but the product with increased unsaturated may be driven out of solution, depleting the supply of active centers. NBE forms very reactive carbenes, even in the presence of weakly activated catalysts. NBE should have been added to these reactions to check if the supply of active centers had been completely depleted when the polymerizations appeared to "die". If any active centers remained, we would have seen a decrease in the amount of NBE present.

The next logical steps in this study were a change of catalyst to the $Re_2O_7/SnMe_4/Al_2O_3$ system and some copolymerization studies. These variables allowed us to address the major issues brought to light in the homopolymerizations discussed above: product solubility and the non-metathesis type reactions between the initial products and the catalyst.

Homopolymerization of DCCB with $Re_2O_7/SnMe_4$. Homopolymerizations with DCCB were continued with the $Re_2O_7/SnMe_4/Al_2O_3$ system in anticipation that it would not react with the original metathesis polymer to form the same conjugated and insoluble species seen with $WCl_6/SnMe_4$. The Re_2O_7 system is considered one of the most versatile of the metathesis catalysts because it displays minimal air sensitivity, is straight-forward to prepare and to store and is applicable to the metathesis of a number of different types of olefins, including those containing functional groups.[14-18] The $SnMe_4$ component in this system acts as an activator. It reduces the Al-Re species to a favorable oxidation state and stabilizes O_2^- groups at the active sites. These can then extract electrons from lower oxidation state Re atoms, and produce the Re^{4+} and Re^{6+} species which are reported to catalyze metathesis reactions.[19]

Polymerization of DCCB with a recently tested batch of catalyst (Monomer/Re_2O_7 ratio = 20/1) produced a fine black precipitate interspersed with the white alumina support. After 20 h, 17% of the monomer had been consumed relative to the internal standard. The black powdery product appeared identical to that observed with the $WCl_6/SnMe_4$ system. It was significant that the products were similar with both catalyst systems because we assumed that the uncontrolled elimination of chlorine from the initial metathesis product was related to the specific chemical interactions between $WCl_6/SnMe_4$ and the initial metathesis products. The disappearance of DCCB was distinctly slower than 1,5-COD, similar to the situation we observed with the $WCl_6/SnMe_4$ system.

The black powder was not isolated from the alumina support and analyzed to confirm that it was identical to the material produced in the $WCl_6/SnMe_4$ polymerizations or that it was formed by a metathesis mechanism. However, it was clear that these homopolymerizations were not producing materials in the solubility range required for processable precursors. If these were ring-opened metathesis products, then the alternating acetylene-dichloroethane copolymer structure of the initial metathesis product was intrinsically unstable under these reaction conditions, and the transformation to polyacetylene could not be controlled.

A further difficulty with the $Re_2O_7/SnMe_4$ catalyst came to light when a "control" polymerization was run to determine the effects of the interaction of DCCB with an alumina surface which had been impregnated with plain water instead of aqueous NH_4ReO_4. Surprisingly, 39% DCCB was consumed in the presence of plain Al_2O_3, and a new GC peak appeared at the same retention time as that expected for 1,4-dichloro-butadiene which is the ring-opened thermal decomposition product of DCCB. This experiment was run under identical conditions to the one in which 17% of the monomer disappeared using a 15% Re_2O_7 loading. The relationship between the amount of DCCB

consumed and the amount of 1,4-dichlorobutadiene produced was not explored further, because these results indicated that at least a portion of the DCCB present was being converted on the naked Al_2O_3 surface to the ring-opened butadiene isomer. The reactions with the "control" catalyst showed that there may be a competition between metathesis and ring-opening decomposition of DCCB with this catalyst.

The $Re_2O_7/SnMe_4/Al_2O_3$ catalyst system has been reported to induce double bond isomerization as well as metathesis at low loadings. These side reactions could be the result of high percentages of Al_2O_3 surface area, as opposed to the correspondingly low Re_2O_7 loadings. At low catalyst loadings, double bond isomerization competes with metathesis reactions using the $Re_2O_7/SnMe_4/Al_2O_3$ system. If this catalyst can decompose DCCB to its ring-opened product, then it could also be reacting with the initial metathesis polymer formed to create a more highly conjugated polymer. The fact that we got a mixture of products from interaction of the catalyst with the monomer introduces the possibility that we were seeing a mixture of products from reactions between the catalyst and the initial metathesis products. The catalysts with low loadings of Re_2O_7 have correspondingly high concentrations of Al_2O_3 and could have increased numbers of side reactions as a result.

Homopolymerization studies with $Re_2O_7/SnMe_4/Al_2O_3$ were abandoned at this point because of the possibility of products mixtures; the insolubility of the product combined with the heterogeneous nature of the catalyst was impractical with respect to product isolation.

Metathesis Copolymerization Studies of DCCB

The next step in our attempt to use DCCB to make soluble conducting polymer precursors was to copolymerize DCCB with another cyclic olefin. Copolymerization would serve several purposes. An aliphatic comonomer would tailor the solubility

characteristics of the product because the ethylene type units would add flexibility to the chains. Additionally, if the dichlorobutadiene units in the initial metathesis polymer were interrupted by saturated hydrocarbon units, then the driving force behind the elimination of chlorine to produce an extensively conjugated system would be decreased. Copolymers which were soluble in the reaction medium would also address the problem of catalyst deactivation when the active site was attached to a polymer which precipitated out of solution. After the elimination reaction was carried out, the final product would be a copolymer of saturated and unsaturated hydrocarbon units which should be more soluble than the partially eliminated homopolymers of DCCB. We could then vary the ratio of the monomer feed for these copolymers and examine at the effect of copolymer composition on the conductivity and the processability of the products.

NBE was chosen as a comonomer because of the high activity of its propagating carbene. The NBE carbene is more reactive for propagation than COD and COE,[20] because the double bond closest to the metal center decoordinates quickly, leaving a "naked" carbene which can easily coordinate more monomer. From previously published work by Patton,[21] we know that COD and cyclobutene react at similar rates because they have the same carbene structures. Although the carbenes for cyclobutene and DCCB are not identical, it is reasonable to assume that the NBE carbene is more reactive than both cyclobutene and DCCB. Patton's work indicated that copolymerization with NBE sped up the disappearance of several monomers which formed less reactive carbenes than NBE, as shown in Figure 3.1. The "hot" NBE carbene might be better at coordinating and reacting with DCCB than the carbene species present in DCCB homopolymerizations, resulting in the incorporation of an increased amount of DCCB into the polymer. Two different types of copolymerization were studied:

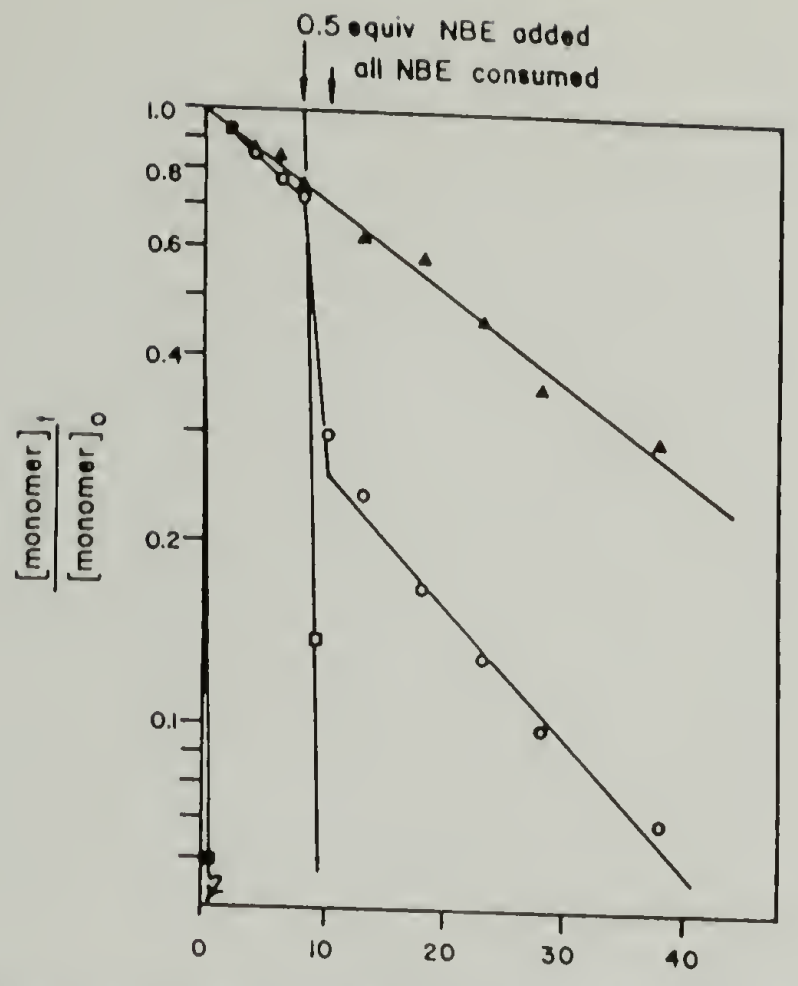


Figure 3.1. Effect of the Addition of NBE on the Rate of Metathesis of the Metathesis of 1,5-COD.

Type I: DCCB was added to the catalyst first, and then NBE was added to see if the rate of DCCB consumption increased.

Type II: Both monomers were mixed together with an internal standard and added to the catalyst.

Copolymerization of DCCB with $Re_2O_7/SnMe_4$. Copolymerization work was initiated with the $Re_2O_7/SnMe_4/Al_2O_3$ system while it was up and running, because it was still a good catalyst for metathesis reactions producing soluble products. Initial experiments with NBE using the $Re_2O_7/SnMe_4/Al_2O_3$ system were disappointing because what appeared to be NBE homopolymers precipitated out of solution almost immediately. Using the Type II conditions described above, a solution of NBE and DCCB (85/15) was added to $Re_2O_7/SnMe_4/Al_2O_3$ at room temperature, with a monomer to Re_2O_7 ratio of 20/1. GC analysis showed that NBE was consumed in the reaction, and that DCCB was not. However, both DCCB and the internal standard were present in such small quantities

relative to the solvent, that it was difficult to draw any conclusion from the data except that DCCB was not consumed quantitatively in the reaction, if at all. More importantly, the reaction showed the importance of controlling the molecular weight of the NBE chains by using a chain transfer agent.

Attempts to make soluble NBE homopolymers using *cis*-2-hexene as a chain transfer agent were not successful with this catalyst system, even when polymerizations were run at 0°C to slow them down and relatively high concentrations of the chain transfer agent as large as 20/1 and 5/1 for NBE/cis-2-hexene were employed. In a typical polymerization, the viscosity of the reaction solution would increase dramatically in the first few minutes, then slowly decrease over the next half hour. Finally the viscosity would increase a second time until the solutions were too thick to sample by GC after about 2 h. It was surprising to find 50% of the NBE remaining in solution after almost 2 h, indicating a lack of accessible or active catalyst.

These results may be due to the heterogeneous nature of the $Re_2O_7/SnMe_4/Al_2O_3$ system. With the $WCl_6/SnMe_4$ system, NBE is consumed in the first 15 minutes of the reaction. The decreased rate of NBE polymerization with the Re_2O_7 catalyst could be caused by a decrease in the number of active catalyst sites as the reaction proceeds, or by the obstruction of the active sites by the growing polymer chains. The latter is more likely in this case, because this catalyst system is a hardy one and does not seem vulnerable to poisons. The changes in the reaction mixture viscosity indicate that some backbiting does occur between the active metathesis centers and the NBE chains. We would not expect poly(NBE) to be vulnerable to backbiting, because of the steric hindrance of the cyclopentane ring, especially with 50% of the monomer still present in solution. However, concentration is a relative term and the local concentration of monomer surrounding the active sites in this heterogeneous system, may be different than the total concentration in solution.

These NBE homopolymerization results explained the fact that DCCB was not incorporated into the polymers prepared by copolymerization between DCCB and NBE. The NBE homopolymers reach high molecular weight quickly and then block DCCB access to the active catalyst sites. Because the chain transfer experiments were less than successful in producing a "well behaved" system for making NBE homopolymers, this heterogeneous system was discarded for the synthesis of DCCB/NBE copolymers. With respect to the $Re_2O_7/SnMe_4/Al_2O_3$ system, monomers other than NBE which are less likely to produce high polymer and block catalytic sites on the surface may be more effective comonomers for future studies.

Copolymerization of DCCB with $WCl_6/SnMe_4$. The chain transfer experiments described above with NBE and *cis*-2-hexene were repeated using the $WCl_6/SnMe_4$ catalyst system at 0°C. NBE disappeared completely in 20 minutes and the polymers stayed in solution. Copolymerizations (Types I and II) were repeated using DCCB and NBE and with *cis*-2-hexene.

As shown in Table 3.3-3.6, the room temperature copolymerization experiments resulted in the consumption of almost 30% of the DCCB originally present after 16 h. Although more DCCB was consumed in the reaction where DCCB and NBE were added simultaneously, we cannot say that DCCB was metathesized more efficiently using this method, because the reactions were not sampled for the same length of time. At the 8.3 h point, 22% had been consumed in both reactions. Although all of the NBE had

Table 3.3. Copolymerization of DCCB and NBE with $WCl_6/SnMe_4$: Type II. (IV-27/Tube A)

Time	CTA/R*	CTA/R**	NBE/R*	NBE/R**	DCCB/R*	DCCB/R**	%DCCB GONE*	%DCCB GONE**
Ref	.18	.15	3.19	2.75	.24	.30		
20min	.14	.13	.07	.06	.20	.29	17%	4%
1.75hr	.08		.04		.20		17%	
13hr		.13		—		.29		4%

Table 3.4. Copolymerization of DCCB and NBE with $WCl_6/SnMe_4$: Type I. NBE at 25 min (IV-27/Tube B)

Time	CTA/R*	CTA/R**	NBE/R*	NBE/R**	DCCB/R*	DCCB/R**	%DCCB GONE*	%DCCB GONE**
Ref	.18	.15	3.19	2.75	.24	.30		
20min	.17		.68		.21		12%	
1.75hr	.14	.07	.02	.01	.20	.28	17%	10%
13hr		.13		.01		.28		10%

Notes: *DC200 used for GC, **AN600 used for GC
R = Nonane CTA = Chain Transfer Agent (*cis*-2 hexene)

Table 3.5. Copolymerization of DCCB and NBE with $WCl_6/SnMe_4$: Type II. (IV-31/Tube A)

Time	cis-2-hexene/ C_9	NBE/C_9	DCCB/C_9	%DCCB GONE
Ref	.15	4.09	.31	
10 min	.12	.05	.28	10%
8.3 h	.06	.01	.24	22%
16 h	.06	.02	.22	29%

Table 3.6. Copolymerization of DCCB and NBE with $WCl_6/SnMe_4$: Type I. NBE added at 20 min. (IV-31/Tube B)

Time	cis-2-hexene/ C_9	NBE/C_9	DCCB/C_9	%DCCB GONE
Ref	.15	4.09	.31	
10 min				
1h	.09	.07	.29	6%
8.3 h	.08	.04	.24	22%

disappeared from these tubes after 10 min, only a 10% and 6% drop in the amount of DCCB present were seen in the two separate trials. Reactions IV-27A and B were run at 0°C to keep high molecular weight NBE from forming too quickly and they showed less DCCB consumed than those run at room temperature. GC analysis using the DC 200 column indicated that 17% was consumed in reactions by both types of copolymerizations after 1.75 h, while sample run on the AN 600 column showed 6% and 10% for copolymerization Types I and II, respectively. The difference in these percentages is probably not significant, because of the small quantities of DCCB present in these copolymerizations (~100mg DCCB in 5 mL of reaction mixture.) As seen in Tables 3.3-3.4, the original ratio of DCCB to nonane (internal standard) was 0.31. The change from 0.31 to 0.22 (29%) shows that a certain quantity of DCCB was consumed, but it is difficult to assert that there is a difference between ratios of .29 and .28 (corresponding to 6% and 10%, respectively). Despite these limitations, these studies did show that the reactive NBE carbene was successful in increasing the amount of DCCB incorporated relative to the homopolymerizations. The results may not be as dramatic as those seen by Patton for nonfunctionalized olefins like COE and 1,5-COD, but when we consider that the homopolymerizations required several days and extra additions of catalyst to exceed 20% DCCB consumption, it is clear that the presence of NBE made a difference.

Norbornene may not have been the best monomer to have chosen for the copolymerizations, because of the difficulties involved in attaining ring-chain equilibrium under reaction conditions. A comonomer like cyclooctene (COE) would provide a more flexible spacer type unit per comonomer than NBE, and would also be closer to DCCB with respect to carbene reactivity. The copolymers would be more likely to be random using COE. Ideally, we would like to design a system where the ratio of the monomer feed determines the composition of the copolymer. Control of copolymer composition is

essential for studying the effect of copolymer structure on the conductivity and processing properties.

Copolymerization with NBE probably resulted in block-like copolymers which would not be as effective in interrupting the extended sequences of poly(DCCB). These DCCB blocks may have been equally as prone to elimination in the presence of catalyst as were the DCCB homopolymers. The extended conjugation in these blocks may also have driven the copolymers out of solution. A monomer like COE with carbene reactivity closer to that of DCCB would be more successful in addressing both these aspects of DCCB polymerization.

Discussion

The results that we have presented forced us to evaluate whether our reaction conditions and protocols were adequate to support productive metathesis. The conditions that were used with each of these catalyst systems were well within the bounds of those reported by other research groups. These conditions have substantial precedent with regard to temperature[5-7] and catalyst to monomer ratios.[5,7,22-27] There are several ways to combine catalyst components and monomers, but our method of adding the $SnMe_4$ to the WCl_6, aging 20 minutes and then adding the monomers worked well in our group for other monomers,[2829] and it also has a solid basis in the literature.[30] Side reactions may be more likely between catalyst species and the growing polymer chain at the higher concentrations of catalyst (25/1 monomer to catalyst), but the black insoluble product was also formed at the lower concentration (200/1) and with the heterogeneous rhenium system as well (220/1).

Despite the care taken to dry and store the different catalyst components and reaction solutions, these experiments were tough to run consistently. Catalyst stability and active species concentration are difficult to control when each solution has the ability

to affect the reaction rate and monomer conversion, and some researchers advocate the use of adventitious water as a cocatalyst.[31-33] However, by patiently repurifying the different reaction components in a logical sequence and repeating the experiments, it was possible to develop an instinct as to whether conditions were sufficiently rigorous to support olefin metathesis.

A second obvious question to raise was whether the products that we saw were ring-opened metathesis products. The convention established in the literature was that at least two methylene groups between the metathesizable double bond and the functional groups were required with homogeneous catalyst systems. Brunthaler's cross-metathesis experiments with DCCB and diisopropylcyclobutene clearly showed that 3,4-substituted cyclobutenes would form metathesis products. We have to conclude that the metathesis polymer formed in the case of DCCB was not stable enough under reaction conditions to remain a precursor to PA.

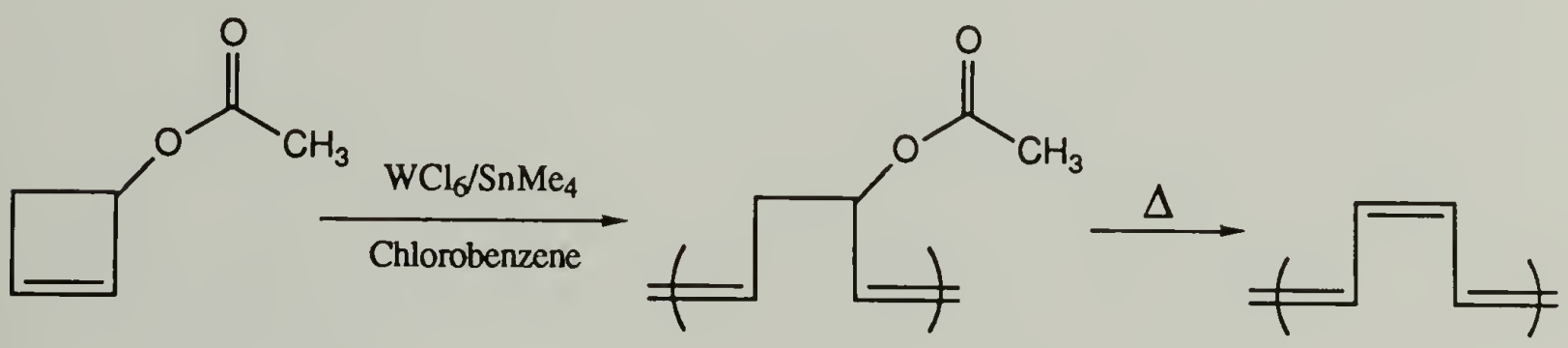
Conclusions

Using the $WCl_6/SnMe_4$ and $Re_2O_7/SnMe_4/Al_2O_3$ catalyst systems, the DCCB polymerization studies described above consistently produced a black, intractable powder, that has been characterized as a partially chlorinated form of polyacetylene. This material was not an adequate precursor to polyacetylene. It was insoluble and the transformation from poly(DCCB) to polyacetylene was not controllable under reaction conditions. Additional experiments could be carried out to show quantitatively that the black solid formed in these reactions was the metathesis product of the ring-opening polymerization of DCCB, but clearly this was not the method of choice for making soluble precursors to conducting polymers. The well characterized catalysts developed by Grubbs and Schrock among others might be more compatible with these functional group-containing monomers and also might provide better molecular weight control. Despite the potential advantages of these new catalysts, we redirected our efforts toward other monomers which would

produce latent conducting polymers, because we had already invested time into learning to manipulate the more traditional Re_2O_7 and WCl_6 systems.

Metathesis Polymerization of 3-Acetoxycyclobutene

Previous results with DCCB were promising because they indicated that 3,4-substituted cyclobutenes would form metathesis products, despite the reported requirement of a two methylene separation between the metathesizable double bond and functional group. However, the uncontrolled elimination of chlorine from poly(DCCB) to form a partially chlorinated polyacetylene rendered this approach inadequate for the synthesis of PA from a processable precursor of poly(DCCB), and we selected ACB as our next target monomer. The metathesis polymer expected from 3-acetoxycyclobutene (ACB) is shown in Scheme 3.4 and should be stable under reaction conditions because the elimination to form polyacetylene occurs via a syn-pyrolytic mechanism. Poly(ACB) would not have the same specific interactions with the metathesis catalysts as halogenated polymers such as poly(DCCB), and it should not undergo the same elimination reactions which led prematurely to polyacetylene.



Scheme 3.4. Metathesis of ACB and Elimination to PA.

Because of the difficulties encountered with product isolation using a heterogeneous catalyst, the $WCl_6/SnMe_4$ catalyst system was used in the studies discussed below. If heterogeneous catalysts were considered, then the $Re_2O_7/SnMe_4/Al_2O_3$ system would have been an obvious choice due to its reputation for compatibility with oxygen containing functional groups. However, doing a small number of "results guaranteed" experiments with a heterogeneous system was a risky option with the small amount of monomer available, especially when the solubility of the reaction products was questionable. We used the homogeneous $WCl_6/SnMe_4$ system because of the numerous reports of metathesis reactions of olefins with ester[5,7,34-37] and ether[38] groups using this catalyst.

Preliminary Studies

The synthesis of 3-acetoxycyclobutene, using the procedure as reported by Cope and Wiberg[39-41] is detailed in the experimental section. The products of the small scale synthesis of ACB were combined and used for scouting polymerizations with $WCl_6/SnMe_4$. The homopolymerizations were designed to see if ACB was consumed in the presence of $WCl_6/SnMe_4$. Copolymerizations were also run with NBE to see if another monomer could be metathesized in the presence of ACB and vice-versa. The monomer solution used in these preliminary studies was 0.13 M in ACB and 0.10 M in nonane and contained 1-acetoxybutadiene (0.03 M) as a major impurity. High concentrations of catalyst were used in these reactions, because ratios of $WCl_6/SnMe_4$/Monomer of 1/3/10 to 1/3/30 were reported in the metathesis of other systems containing esters.[38] $WCl_6/SnMe_4$ ratios of 1/2 were also prevalent.[24] Larger ratios of tungsten to monomer (1/3/100) were not effective in the presence of functional groups.[38] Although some groups reported higher temperatures for the metathesis of functional group-containing olefins, we were hesitant to run reactions at temperatures

higher than 50°C because of the possibility of the pyrollytic elimination of the acetate group. The results of the initial polymerization studies are shown below in Table 3.7.

Table 3.7. Initial Metathesis Polymerization Reactions of ACB with $WCl_6/SnMe_4$. Scouting Experiments.

Reaction	WCl_6:$SnMe_4$: ACB	Temperature ℃	Method	Comonomer	Monomer Consumed after 24hrs
III-87	1 : 2 : 27	18	A*	—	0%
III-88	1 : 2 : 13	50	A*	—	15% ACB
III-89	1 : 2 : 13	50	A*	NBE	24% ACB 65% NBE
III-91	1 : 2 : 13	50	A*	NBE	49% ACB 20% NBE
III-92-1	1 : 2 : 13	50	B**	—	40% ACB
III-92-2	1 : 2 : 13	50	B**	NBE	58% ACB 86% NBE

* Monomer added after 20 minute aging period.
** $SnMe_4$ added last

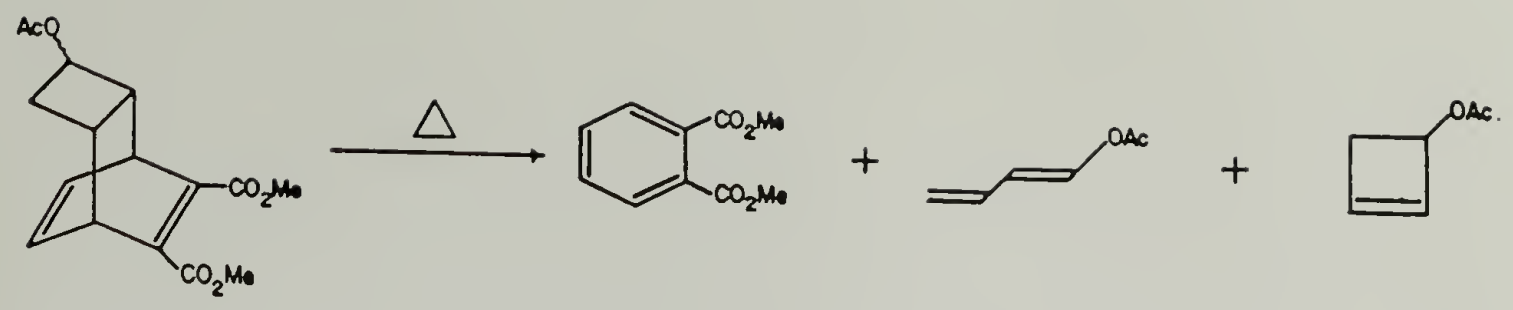
In experiments III-87-91, a solution of ACB and nonane, an internal standard, was added to the red-brown catalyst mixture of WCl_6 and $SnMe_4$. Over the course of an hour, the reaction mixture changed from the original red-brown color to a greenish brown color usually associated with this catalyst system when it was no longer active. In the last two experiments (III-92-1,2) the monomer/internal standard solution was added to a solution of WCl_6 in chlorobenzene and then the $SnMe_4$ component was added last. Both reaction solutions turned green immediately after the cocatalyst addition, changing to a bright blue color after one hour.

Although the products of these small scale reactions were not analyzed, the GC data in Table 3.7 does indicate that more ACB is consumed with NBE as a comonomer than in the ACB homopolymerizations. The disappearance of NBE was considerably slower in the presence of ACB than in homopolymerizations with the same catalyst. Side-by-side control reactions with NBE were not run for these experiments, but in a typical homopolymerization with $WCl_6/SnMe_4$, NBE disappears in minutes. In these reactions, 14-80% NBE remained even after several hours. Since the polymerization of NBE was slower in the presence of ACB, it is likely that both monomers are reacting at the same active centers, and that ACB was effectively tying up these centers and retarding NBE polymerization in the process. Since we had seen only ring-opening polymerization with NBE using the $WCl_6/SnMe_4$ system, we were optimistic that ACB was also reacting at these centers to produce ring-opened metathesis products.

The small concentration of both the monomer and the internal standard in these polymerizations made it difficult to analyze the products and draw conclusions about the mechanism by which ACB was consumed. Subsequent experiments were designed such that concentrations were higher, and the reactions were run in tubes with teflon stopcocks (as opposed to o-ring seals) to avoid the the possibility that the concentration of the reactants was changing due to evaporation from the tubes or to absorbance by the o-rings. Use of an auto sampler improved the precision of the GC measurements.

Larger Scale Metathesis Studies with ACB

The results of these initial studies were promising enough that we proceeded to synthesize ACB on a larger scale to facilitate analysis of the metathesis products. Unfortunately, the pyrolysis step (see Scheme 3.5) was not straightforward to scale up.



Scheme 3.5. Pyrolysis of Dimethyl 3-Acetoxytricyclo[4.2.2.$0^{2,5}$] deca-7,9- diene-7,8-dicarboxylate

We tried several different sets of conditions and configurations for the pyrolysis reaction, but the side products from this step were difficult to separate from ACB and yields were correspondingly poor. As described in the experimental section, Wiberg et. al.[39] removed the 1-acetoxybutadiene formed in the pyrolysis step by forming a Diels-Alder adduct between maleic anhydride (MA) and the diene. The reaction was carried out with neat ACB as the solvent and the adduct was precipitated as the silver salt. Excess amounts of MA were added to drive the reaction to completion, but both the MA and the silver salt were difficult to separate from ACB on the relatively small scales used. Rather than bring up more starting material to further optimize the pyrolysis steps, we opted to continue the metathesis experiments with the materials available.

In a typical homopolymerization, the catalyst mixture turned a deep red color, bordering on dark purple when the $SnMe_4$ was added to the WCl_6. Table 3.8 lists the experimental conditions for the ACB homopolymerizations.

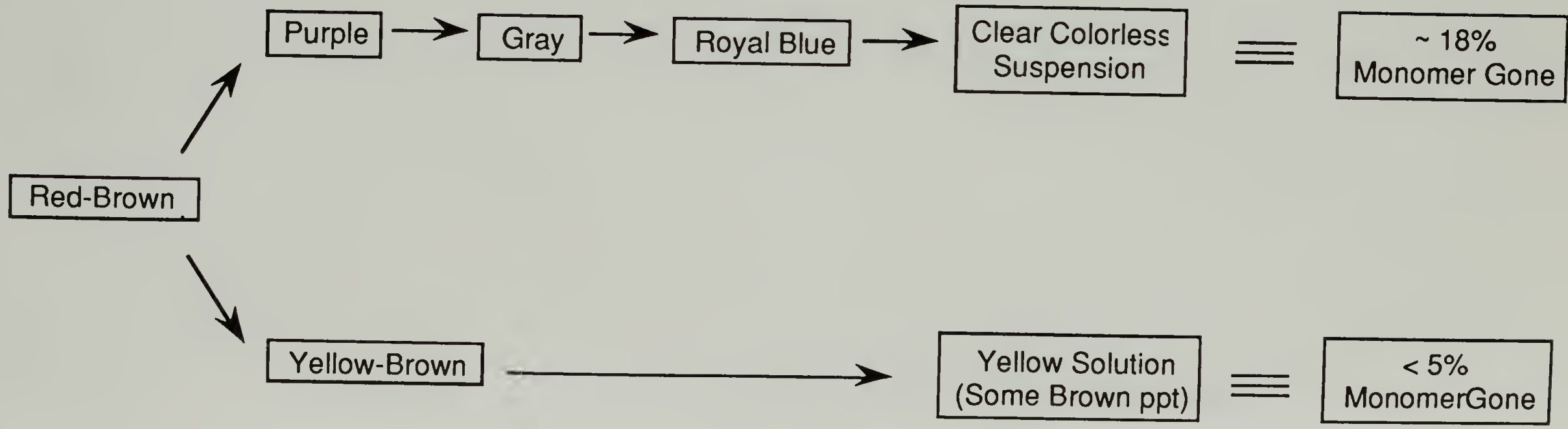
Addition of the monomer produced either a yellow-brown color or a brilliant purple color which faded to a metallic gray after 0.5 h. Scheme 3.6 shows the reaction pathways which resulted from these initial reaction solution colors. After eight hours, the final solution in the latter case was a royal blue color when stirred. Upon standing, a fine blue precipitate settled to the bottom, leaving a clear colorless mother liquor. In the case of the brown solution, GC analysis showed no disappearance of ACB from the reaction

mixture, relative to the internal standard. An average of 18% of the monomer was consumed in the bright purple reactions, while less than 5% was consumed in reactions whose coloration was somewhere in between the two. With this catalyst system, red is usually indicative of an active catalyst, while a blue colored catalyst does not usually produce any metathesis products. The purple color could be considered a combination of the two.

Table 3.8. Metathesis Reactions of ACB with $WCl_6/SnMe_4$.

Reaction	Molarity in ACB		Monomer added	Monomer Consumed
(Ntbk IV)	Monomer Solution	Reaction Mixture	(Volume)	(%)
IV-71	0.6*M*	0.3*M*	0.30 mL	15.4
IV-73	0.6*M*	0.3*M*	0.30 mL	21.7
IV-75	0.6*M*	0.3*M*	0.30 mL	NR
IV-79	1.1*M*	0.5*M*	0.20 mL	4.2
IV-85A	1.1*M*	0.6*M*	0.25 mL	2.3
IV-85B	1.1*M*	0.5*M*	0.15 mL	16.8

Previous experience with this catalyst system led us to correlate catalyst color with activity. Red and red-brown colors were typically healthy reactions, and green and blue colors usually indicated dead catalysts. Surprisingly, in III-92 and in the experiments listed in Table 3.8, monomer disappeared from bright blue solutions. One could argue that only a few active centers are needed and that these may not be numerous enough to keep the reaction solution red colored, but this seems unlikely. Alternatively, the disappearance of monomer and the change in color could be a result of ACB binding irreversibly to the tungsten centers to form a blue colored complex. In the case of the



Scheme 3.6. Color Scheme for Metathesis Reactions of ACB with $WCl_6/SnMe_4$

brown solutions, other impurities present in the reaction solutions may have blocked complexation sites on WCl_6 because they made better ligands than ACB.

Using 300 MHz ^{1}H-NMR, each of the components of the reaction mixtures from IV-71 and 73 was examined for evidence of metathesis products and of monomer decomposition to the 1-acetoxybutadiene. The lower and higher boiling fractions of the metathesis reaction mixtures were crudely separated by trap to trap distillation after several freeze pump thaw cycles. The clear, colorless distillate was diluted with the benzene-d_6 to make NMR samples. The dark blue solid left in the tubes after distillation was stirred with benzene-d_6 overnight to extract the soluble residues for NMR analysis. Any high boiling oligomers or polymers should be found in the residues which remained in the flasks after distillation. Low molecular weight products and residual monomer would be found in the trap to trap distillate, and the composite reaction solutions should contain both. NMR was used to analyze the products because the vinyl protons of the ring-opened metathesis polymer of ACB should be in a significantly different electronic environment than the cyclobutene vinyl protons. The same should be true of the protons on any 1-acetoxybutadiene formed via the decomposition of ACB. The peak representing the reaction solvent (chlorobenzene) was decoupled for these spectra to emphasize peaks from the reactants and products The trap to trap distillate was a clear colorless liquid in both of the reactions analyzed; no new peaks due to products were evident in either sample. In fact, NMR spectra of the reactions where monomer was consumed looked identical to those in which no reaction was seen by GC. No evidence of metathesis products was seen in either the samples from the composite reaction mixtures or from the soluble components of the higher boiling residues remaining in the reaction tube after distillation.

Although the NMR did not confirm the presence of metathesis products, this did not mean that none were formed. Because the NMR solutions were dilute, the peaks

representing the vinyl protons were small and if less than 18% of the monomer was reacted, the product vinyl peaks may have been small enough to be below the noise level. Additionally, once stripped of solvent under vacuum, any polymeric or oligomeric metathesis products which formed may not have been easily redissolved in deuterated benzene.

Some crude gravimetric measurements were also done in conjunction with these studies. The tubes for reactions IV-77, 85A, and 85B were tared before adding catalyst mixtures or monomers. After the metathesis reactions were complete and the lower boiling components had been removed using trap-to-trap distillation, the tubes (still containing the high boiling residues) were reweighed. When the final weights of the tubes for reactions IV-85A, B were compared to the tare weights, the samples lost 2 and 4 mg, respectively. In IV-77, no monomer was consumed and the tubes were not reweighed. Even if the tubes had only contained catalyst residues, mass gains in the range of 2-6 mg would be expected for these experiments, based on the amounts of catalyst originally added to the tubes. If polymeric products have been present, the mass gains would have been larger. On the other hand, we may not have seen mass changes of this magnitude because the weight of the tubes limited these measurements to the four digit range of the Mettler balance. In addition, these values were based on a single tare weight for each tube. For weight changes of this magnitude, the tubes should be weighed several times, both before and after reactions on a more accurate scale. Because of these limitations, results from these gravimetric experiments should not be considered conclusive.

Discussion of ACB Metathesis Experiments

All of the observations discussed above indicated that metathesis products were not formed in these reactions. There were no indications of oligomers by GC, the reaction solutions did not increase in viscosity and only small amounts of monomer were

consumed. In addition, reaction solution colors were not indicative of those which typically produce metathesis products with the $WCl_6/SnMe_4$ system. Note: The analysis of the products done here may not have been sufficient to detect metathesis products even if they were present. Both the reactions themselves and the NMR studies dealt with small concentrations of monomer, and the concentration of the products may have been too small to characterize with the methods used.

If we assume that no metathesis products were formed, these results provoke two questions:

1) What happens to the ACB that is consumed during the polymerizations?
2) Why doesn't ACB undergo ring-opening polymerization in the presence of this metathesis catalyst?

In response to the first question, if the disappearance of monomer from these polymerizations was not due to the formation of metathesis products, then ACB could be complexing with WCl_6 or $SnMe_4$, rendering the system ineffective for producing metathesis products. This would explain both the amounts of ACB consumed and the lack of metathesis products. Perhaps ACB remains coordinated to the tungsten carbene species and no other monomers can coordinate, or the reaction with ACB may change the electronic configuration of tungsten such that it cannot form a metathesis carbene.

We calculated the moles of ACB consumed per mole of WCl_6 present in solution to see if the values obtained were in the right range if indeed the monomer had complexed with the catalyst (see Table 3.9). If 100 moles of cyclobutene had been consumed per mole of WCl_6, then all monomer consumption could not be due to complexation, but this was not the case. The numbers range between 2 and 7 equivalents of ACB per mole of WCl_6 present, and these are reasonable values to expect if ACB had complexed with the tungsten.

These calculations should be considered a rough estimate because they were based on GC results which were not normalized for the response factors of ACB and nonane, the internal standard. The uncertainties in the determination of catalyst and monomer

Table 3.9. Moles of ACB Consumed per Mole of WCl_6 Present Initially.

Reaction	Moles ACB
IV-71	5.2
IV-73	7.5
IV-75	NR
IV-79	1.7
IV-85A	1.2
IV-85B	5.4

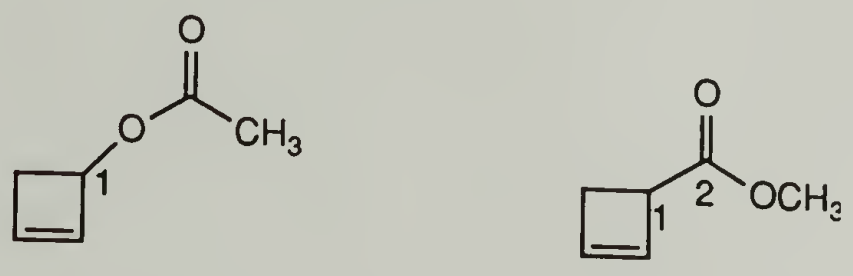
concentrations also contributes to the errors in these calculations. Monomer solution concentrations were determined by GC and although the injection port temperatures were lowered from 200°C to 160°C for these reactions, there still may have been some pyrolysis of ACB and subsequent decomposition to 1-acetoxybutadiene. This could distort the percentage amounts on the GC report because the amount lost at the injection port is more of a function of flow rate and residence time than of the volume of ACB present in the sample. An accurate GC calibration is needed if one wants to accurately determine how many moles of monomer are involved. The catalyst concentrations used in these calculations provide an additional source of error, because although the $WCl_6/SnMe_4$ system is considered homogeneous, it is not clear what percentage of the WCl_6 molecules

are actually in solution. To complicate matters further, there is probably a difference between the number of WCl_6 molecules which are active for metathesis and those which are available to form organometallic complexes. In any case, the ratios shown in Table 3.9 indicate that it is not unreasonable to think that the monomer which was consumed reacted with the catalyst to form non-metathesis products.

The most convincing piece of evidence for ACB/WCl_6 complexation is derived from the fact that the bright blue colored product solutions from these reactions were actually suspensions of a finely divided solid which settled to the bottom of the reaction tube overnight. In our experience, solutions of WCl_6 in chlorobenzene never separated and became colorless, even after standing for several months. This behavior indicated that there had been a fundamental change in the chemical composition of the catalyst; the blue particulate solid represented some sort of $WCl_6/SnMe_4$/ACB complex. In some of the preliminary experiments (III-91-1,2) where the $SnMe_4$ component was added last, the solutions turned blue faster and we saw monomer disappear via GC from blue solutions. In hindsight, it becomes clear that a greater percentage of ACB disappeared from these reactions because the WCl_6 was more open to complexation without the $SnMe_4$ component present to interfere. The solutions turned blue sooner because the ACB molecules were complexing sooner.

The second question prompted by these studies concerns why ACB does not undergo metathesis reactions with this catalyst system. These results are consistent with the previously discussed concept that homogeneous metathesis catalysts such as $WCl_6/SnMe_4$ are tolerant of functional groups, as long as they are at least two methylene carbons away from the double bond. In the case of ester groups however, it has been shown that an additional carbon may be required between the ester oxygen and the double bond,[6,38] depending on the direction that the ester group faces; the position of the oxygen linkage on the ester group is critical. Metathesis of esters with the double bond in the

alcohol fragment (alkenyl esters) can be more difficult than if the oxygen atoms are separated from the double bond by the carbonyl carbon. As shown in Scheme 3.7 ACB has only one carbon atom between the double bond and the ester group, and the ester oxygen is bound to the cyclobutene end of the molecule.



Scheme 3.7. Ester-Double Bond Separation in ACB.

Both the close proximity of the oxygen atom (n=1) and the connectivity of the ester to the cyclobutene moiety may have been a problem in these studies. We had hoped that when coordinated, the cyclobutene ring would keep the ester group separated from the metal center, but our results indicate that the ester group did react with the tungten carbene before metathesis could occur. Given these results, the $Re_2O_7/SnMe_4$ on alumina catalyst reported by Mol for the metathesis of allyl acetate would be a better catalyst choice for ACB in future studies.

The failure of ACB to undergo ring-opening polymerization in the presence of $WCl_6/SnMe_4$ may be due to other reasons besides the close proximity of the acetoxy group to the double bond. Functional groups have been reported to have a variety of undesirable effects on olefin metathesis and there may be factors particular to the ACB system which inhibit constructive metathesis. Water or acid could be destroying the WCl_6 centers, making them useless for metathesis, but available to complex with ACB. Verkuiljen reports that the presence of free acid in the metathesis of esters with $WCl_6/SnMe_4$ can

poison the catalyst, if it is present in excess of the amount of WCl_6.[42] Acetic acid, formed by the decomposition of ACB, could also be acting as a catalyst poison.[43] Alternatively, if the monomer solutions were not dry enough, water could be present and it has been reported as both a cocatalyst and a catalyst poison for metathesis systems.[31-32] The driving force behind catalyst deactivation from these impurities can be the formation of oxo-metal bond.[33] The catalyst centers which haven't been deactivated by complexation with ACB molecules could have been destroyed by either water or acetic acid present in the system, although the quantities of these impurities should not have been high.

Conjugated dienes have also been reported to deactivate these types of systems, and 1-acetoxybutadiene was certainly present in these reactions as a decomposition product of the pyrolysis reaction in the ACB synthesis. The diene moiety may coordinate so tightly to the tungsten center that no ACB molecules can approach. There may have been a competition between complexation and metathesis at the tungsten centers, and the fraction of metathesis products may have been small enough that they were not seen.

Conclusions

The preliminary experiments looked promising for the metathesis of ACB for use as a soluble precursor for polyacetylene, but these results were misleading. When the experiments were done on larger scales and under more carefully controlled conditions, the percentages of monomer which disappeared were in the range of 20% for any given reaction. Copolymerizations were not done with the latter set of reactions due to the small amount of monomer available, but copolymerization with NBE could show if any active centers remained in the blue solutions, if the NBE was added last. Cross metathesis with an acyclic olefin could show whether any ring-opened products were formed. The larger percentages of monomer consumed in the scouting reactions could have been due to absorption of monomer by the o-ring seals or leakage from the same. There could have

been a greater proportion of active centers in these reactions or a correspondingly smaller number of impurities.

Although no evidence of metathesis products was observed with the analysis methods used, we cannot say definitively that none were formed. The products may have been too high in molecular weight to see by GC and too low in concentration to see by NMR. GPC analysis of these reactions would be helpful in seeing the formation of oligomers, but as a general statement, the experiments need to be done with higher concentrations of monomer to give correspondingly higher concentrations of the products, in order to facilitate product analysis.

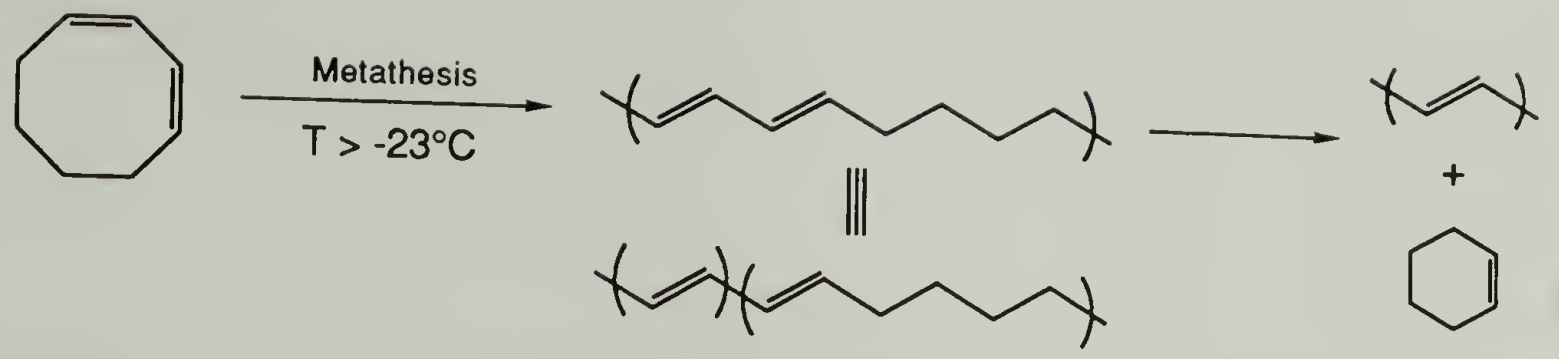
These experiments do not prove that ACB cannot be metathesized, but they do point out the limitations of this particular catalyst system with this monomer. If more monomer had been available, then the $Re_2O_7/SnMe_4/Al_2O_3$ system would have been an obvious second choice, but at the time, the difficulties involved in product separation with a heterogeneous catalyst were not attractive when monomer quantities were limited. In order to ascertain whether the monomer is indeed complexing irreversibly with the catalyst or at least hindering it from performing productive metathesis, one needs more starting material. ACB was surprisingly difficult to synthesize in pure form because of the small scale adopted, but the purification would be more efficient if it was carried out on a larger scale.

Although the experiments described above do not show what happens to ACB in the presence of $WCl_6/SnMe_4$, they do show that the combination of this particular catalyst system and monomer do not provide a convenient route to soluble precursors of polyacetylene. Future experiments should employ the new alkylidene catalysts developed by Grubbs[44-45] and Schrock[46-48] which might be more tolerant of the acetoxy group in close proximity to the double bond. With the right catalyst system, metathesis polymers of ACB would still make exciting latent conducting polymers.

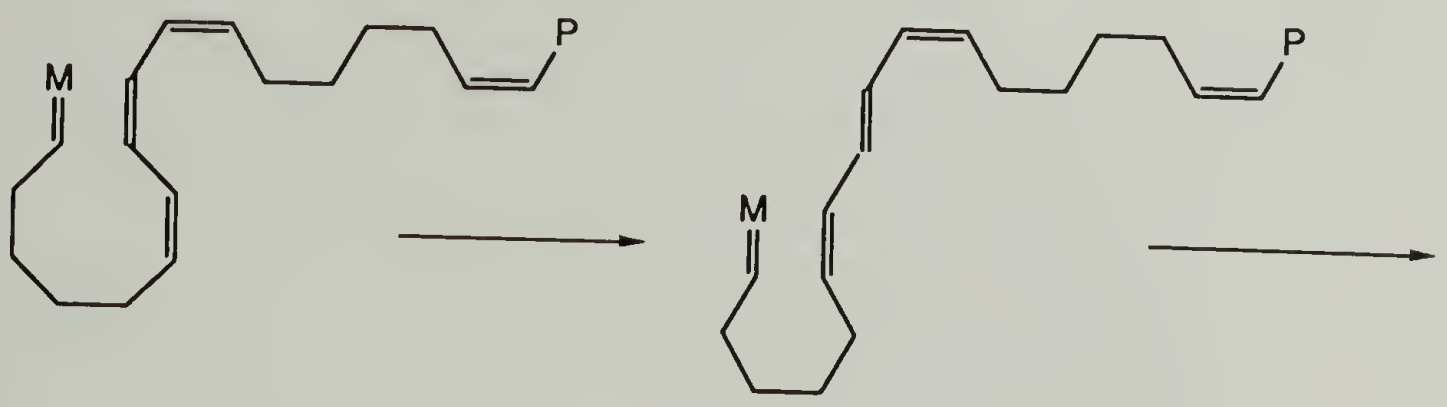
Metathesis Polymerization of 1,3-Cyclooctadiene

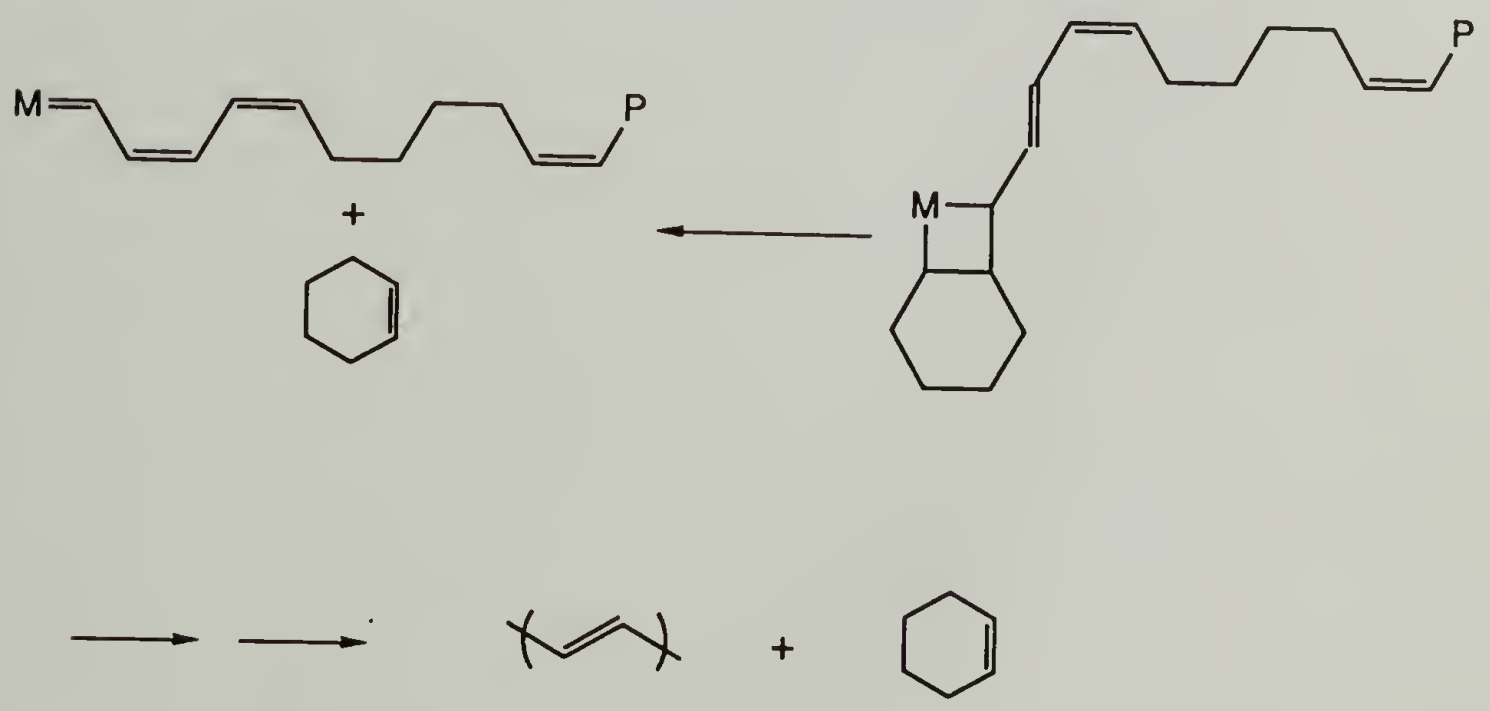
A third method of synthesizing polyacetylene takes advantage of the ability of metathesis catalysts to backbite and react with the polymer chains that they have produced by ring-opening of cyclic monomers. Ideally, the metathesis of 1,3-cyclooctadiene (1,3-COD) produces poly(1,3-COD), an alternating copolymer of acetylene and cyclohexene.[49] Further interaction of the metathesis catalyst with the polymer should ultimately yield cyclohexene and polyacetylene, as shown in Scheme 3.8, if the reaction is run above the ceiling temperature for cyclohexene, which is very low.[50-51] If reactions are run above this temperature, then cyclohexene should not be reincorporated into the polymer. In contrast to the case of DCCB where the subsequent reaction of the polymer with the catalyst led to undesirable results, conditions were tailored in these reactions to promote further interaction between the metathesis carbenes and the polymer chains in order to form new products. We take advantage of the fact that cyclohexene is not susceptible to polymerization under reaction conditions, and the formation of cyclic oligomers from polymerization of 1,3-COD ultimately results in equal moles of acetylene units in the polymer chain and free cyclohexene.

The experiments were designed to produce the maximum amount of cyclohexene possible and to convert the maximum amount of 1,3-COD into polymer. The major experimental variables included adding extra catalyst and using copolymerization as a tool to provide carbenes of different reactivities as well as different types of double bonds for the degradative metathesis reactions which would produce cyclohexene.



Example of Backbiting to Produce CXE and PA





Scheme 3.8. Metathesis Polymerization of 1,3-COD and Extrusion of Cyclohexene via Backbiting Reactions to Produce PA.

Homopolymerization of 1,3-COD with $WCl_6/SnMe_4$

Homopolymerizations of 1,3-COD were studied first. The WCl_6 and $SnMe_4$ catalyst components were combined and aged for 20 minutes unless specified otherwise, before the addition of the monomer/internal standard solution. 1,5-COD was used as a test monomer for each set of metathesis reactions. Typically, 1,5-COD disappeared in the test polymerizations within 20 minutes and the viscosity of the reaction mixture increased visibly. Extra catalyst was added at intervals to insure that an adequate supply of active centers was available, both to increase the degree of 1,3-COD polymerization and to promote the backbiting reactions which would produce the polyene structures. The 1,3-COD homopolymerizations were visibly different from the test runs with 1,5-COD ; no viscosity increase was apparent to the eye, consumption of monomer seemed to level off after each successive addition of catalyst, and a maximum of 70% of the 1,3-COD was converted. When the monomer/standard solution was added to a healthy solution of catalyst, the color deepened to a brownish red and 1,3-COD was slowly consumed. The dark color made it difficult to see if any polymer was precipitating.

Typical GC traces for the starting materials and products of a typical homopolymerization are shown in Figure 3.2. Initially, the presence of even small quantities of cyclohexene was encouraging, because it meant that 1,3-COD was being polymerized and depolymerized by a metathesis mechanism. Unfortunately, the yields of cyclohexene were negligible, even when the reactions were run for days and extra catalyst was added periodically. The relationship between the moles of 1,3-COD consumed and the number of moles of cyclohexene produced is graphed in Figure 3.3 for a typical homopolymerization with the $WCl_6/SnMe_4$ system. The amounts produced were several orders of magnitude less than expected for 100% conversion poly(1,3-COD) to PA. The calculations, detailed in the experimental section, assume that peak areas correspond directly to the amounts of cyclohexene and 1,3-COD, respectively, because a rough

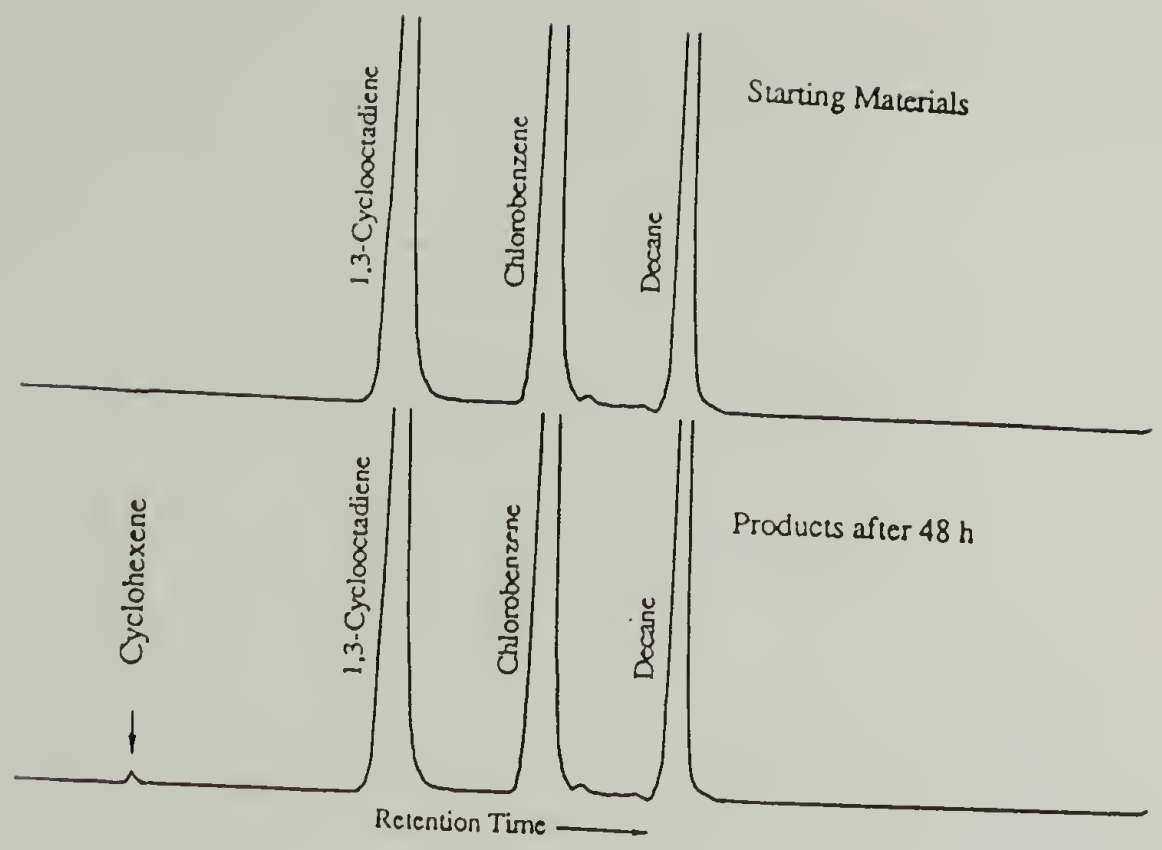


Figure 3.2 Trace of GC Data from 1,3-COD Homopolymerization

determination of the response factors for 1,3-COD and cyclohexene showed that they were reasonably close. (See Notebook Page IV-86.) The response factors could have been determined more accurately, but the results would not have changed the fact that the amounts of 1,3-COD consumed and cyclohexene produced differed by almost three orders of magnitude. The other homopolymerizations were also run for several days and showed similar ratios of cyclohexene to internal standard, as shown in Table XX Appendix XX.

Copolymerization of 1,3-COD with $WCl_6/SnMe_4$

Two problems were evident from the homopolymerization studies discussed above. First, 1,3-COD was not being converted to polymer in the yields expected. Second, the amount of cyclohexene produced indicated that the homopolymer formed was

not susceptible to backbiting. These two issues were addressed separately by two different types of copolymerization.

1) Copolymerization with NBE would supply a highly reactive carbene in order to polymerize more 1,3-COD. If the lifetime of these active centers is time-dependent in the presence of the conjugated 1,3-diene units, then a faster polymerization rate should incorporate more 1,3-COD.

2) Carbenes of 1,3- and 1,5-COD would be more equal in reactivity, but the resulting copolymer might provide better ligands for coordination with the tungsten than 1,3-COD homopolymers, facilitating the formation of cyclic oligomers.

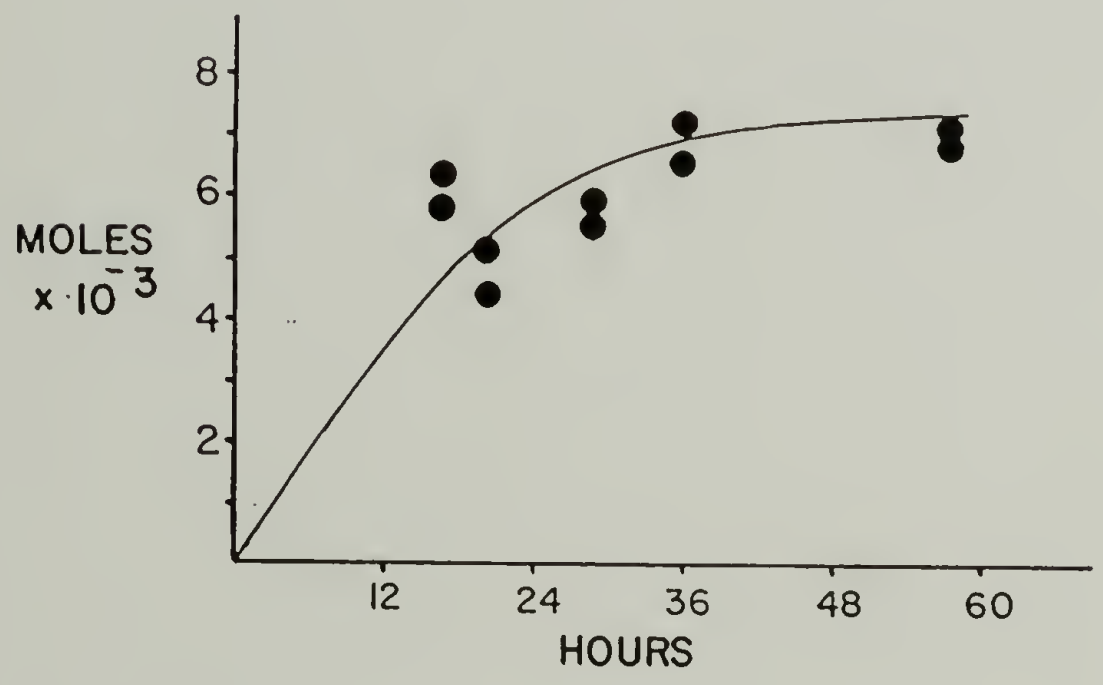
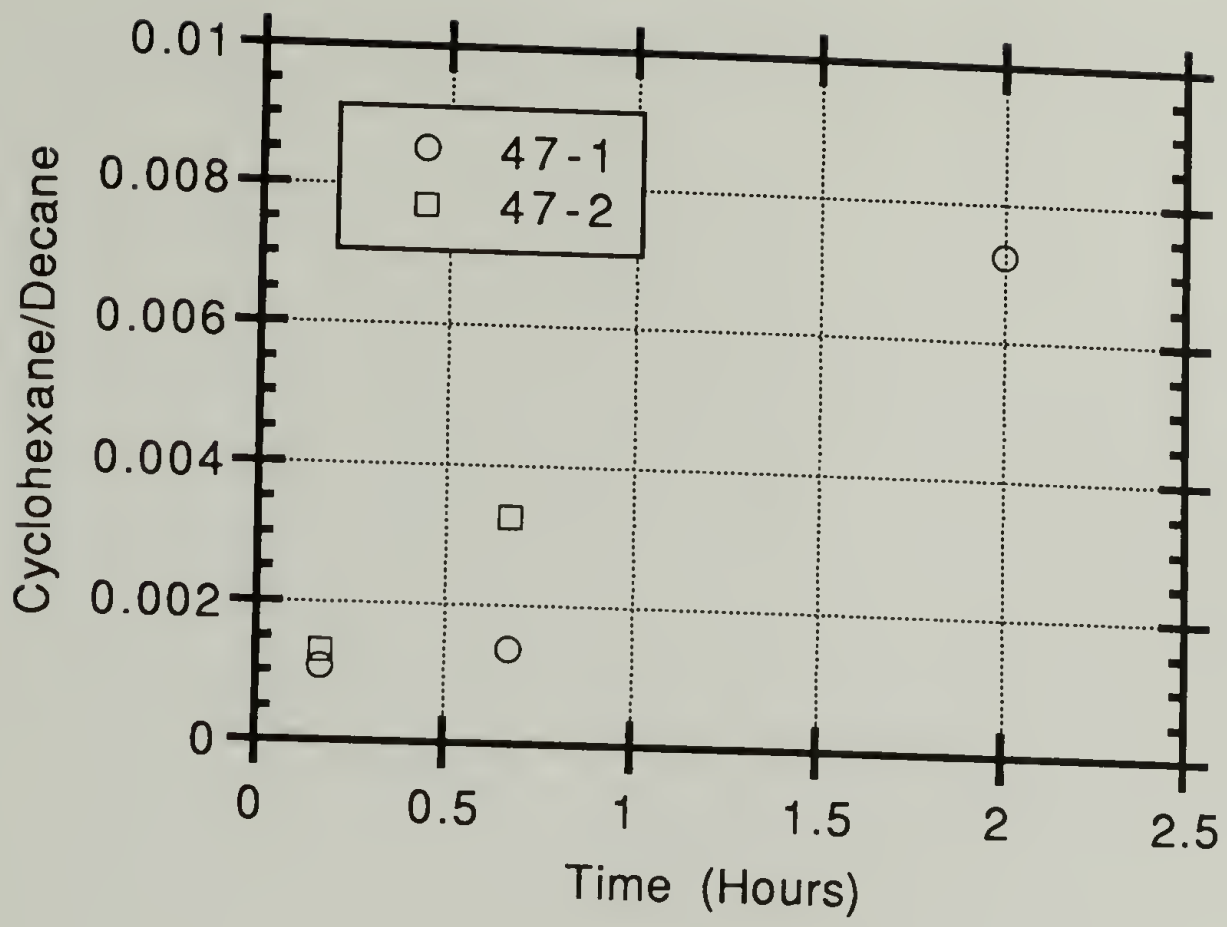


Figure 3.3. Moles of Cyclohexene Produced per Mole of 1,3-COD Consumed in a Metathesis Polymerization.

Copolymerization of NBE and 1,3-COD. If inactivation of the carbene species over the course of the reaction leads to sluggish incorporation of 1,3-COD into the polymer, then the addition of NBE, which forms a highly reactive carbene, to polymerizations in progress should increase the rate of 1,3-COD polymerization and therefore the amount of 1,3-COD included in the copolymer over time. Experiments by Patton and McCarthy showed a dramatic increase in the rate of 1,5-COD polymerization when NBE was added, as shown in Figure 3.1.[21] We hoped to see the same sort of result in the experiments described below. We wanted to polymerize a large percentage of 1,3-COD, so that we could look at backbiting or polymer degradation conditions separately.

As shown by the data graphed in Figure 3.4, and 3.5 and shown in Table 2.5, the addition of NBE to 1,3-COD reactions which were already in progress showed an increase in the amount of 1,3-COD consumption and cyclohexene production compared to the homopolymerizations, but not the dramatic change that we anticipated. Although a greater percentage of 1,3-COD had been consumed at the 2 and 6 h points than in the 1,3-COD homopolymerizations, we did not see the sharp decrease in the amount of 1,3-COD present directly following the NBE addition, as was demonstrated in Patton's NBE/1,5-COD systems. The rate of NBE consumption was correspondingly slower, and in reactions IV-47 and 49, NBE was still present in the reaction solutions after 2 h and 6 h, respectively. In typical NBE homopolymerizations and in copolymerizations with routine comonomers like cyclooctene, NBE systems polymerize and gel almost before a GC sample can be removed. NBE consumption was clearly slower in these reactions than one would expect for NBE homopolymerizations. The corresponding increase in 1,3-COD consumption indicates that metathesis is occurring at the same active centers as 1,3-COD polymerization and that carbenes formed from 1,3-COD are not as reactive.



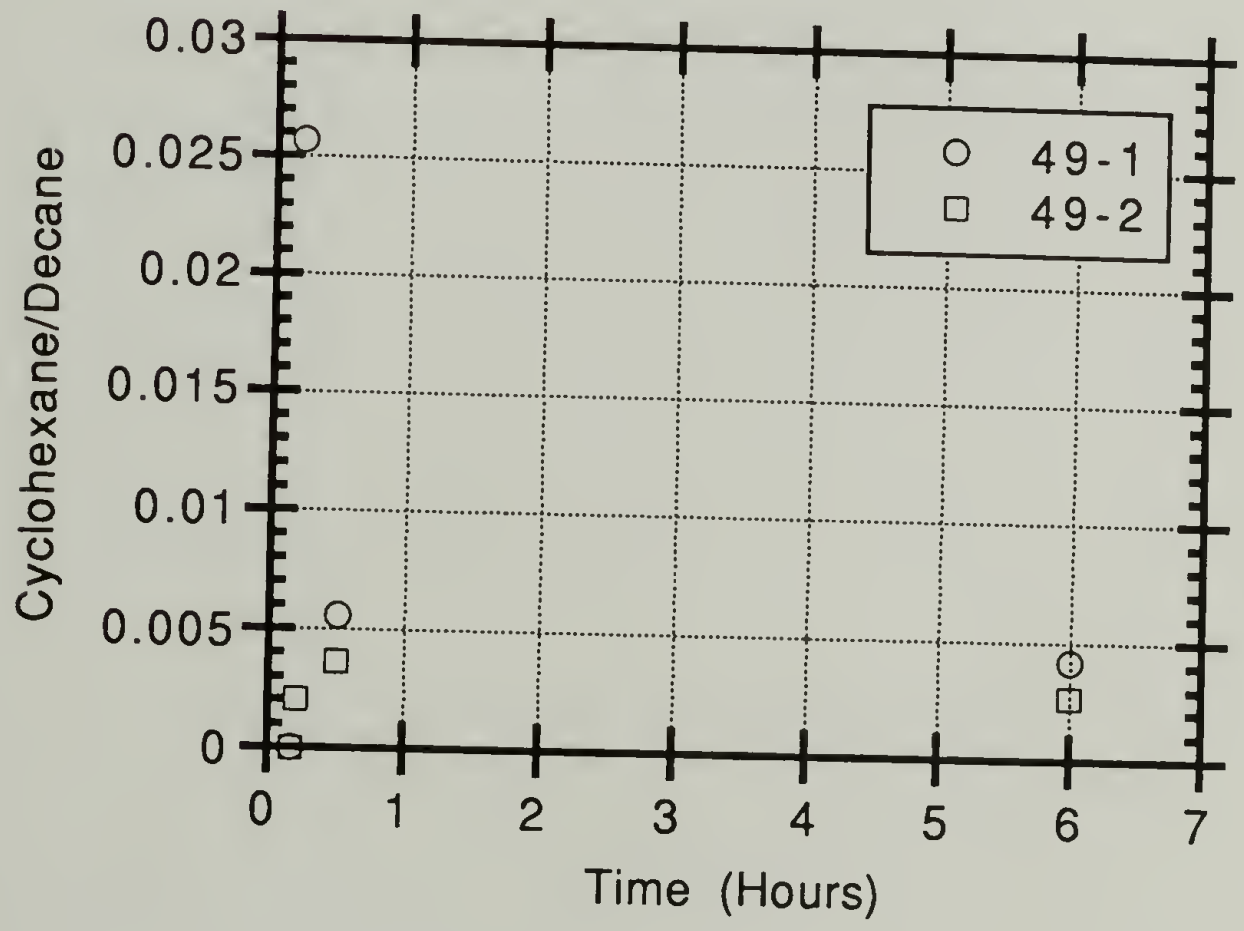
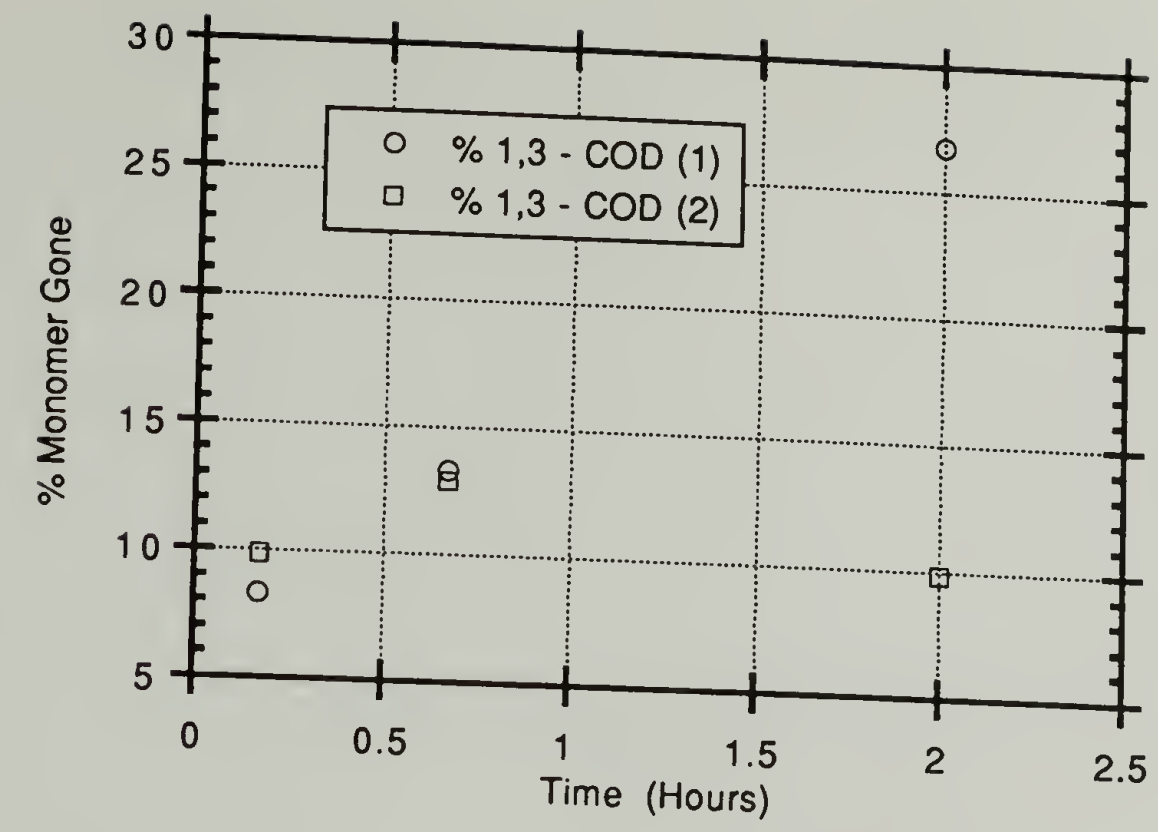


Figure 3.4. Cyclohexene Produced in Type I Copolymerizations of 1,3-COD with NBE. a) IV-47-1,2 b) IV-49-1,2



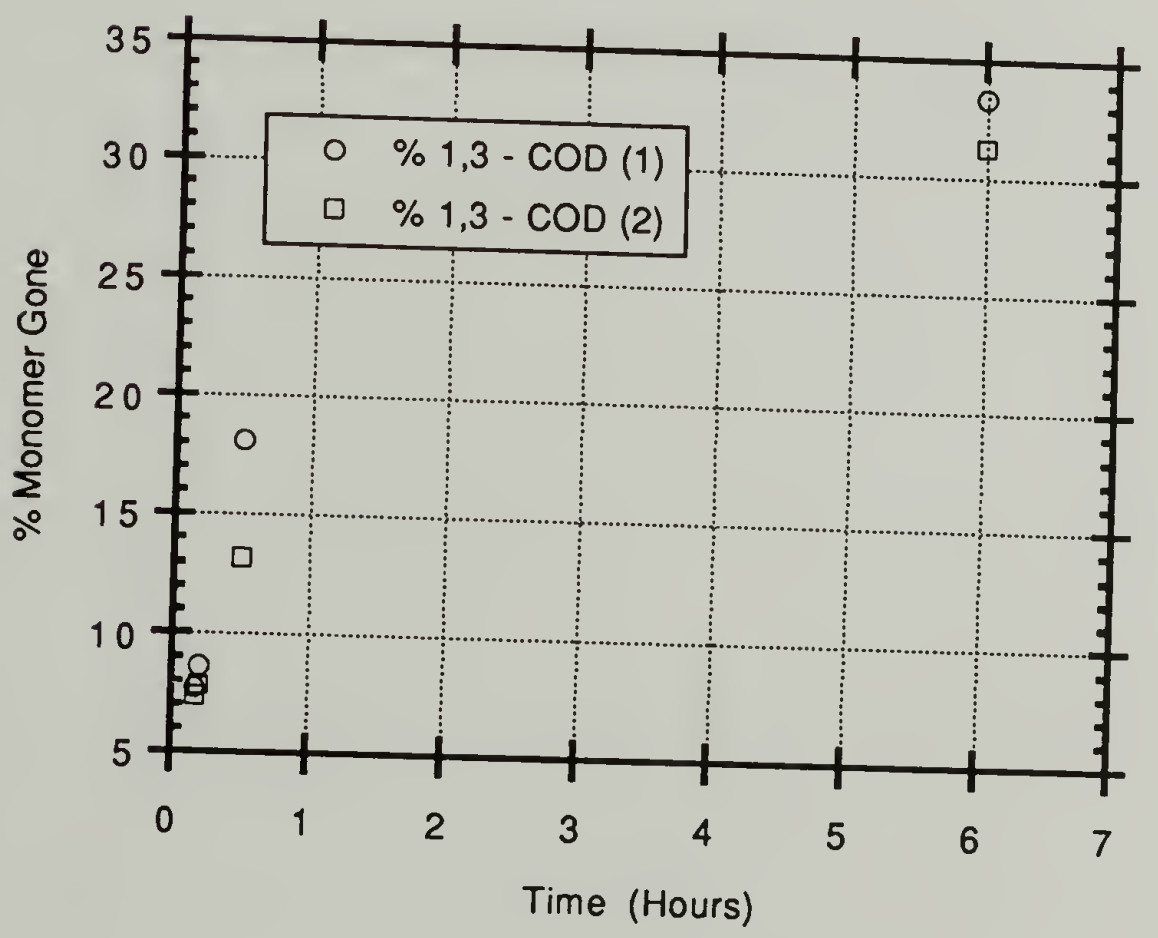


Figure 3.5. Consumption of 1,3-COD in Type I Copolymerizations of 1,3-COD with NBE. a) IV-47-1,2 b) IV-49-1,2

It is difficult to state unequivocally that the rate of 1,3-COD consumption was greater with the addition of NBE, because the data for the homopolymerization reactions was taken over longer periods of time and additional catalyst was not added to the NBE copolymerizations. GC data was only collected up to 2 and 6 h respectively for reactions IV-47 and IV-49 because they became too thick to sample and there was no reason to expect any difference between this situation and the homopolymerizations described earlier. These marked increases in solution viscosity were in direct contrast to 1,3-COD homopolymerizations, where solution viscosity was constant throughout the reactions.

Copolymerization of 1,5-COD with 1,3-COD. Coordination with the 1,5 oligomers should help to keep the catalyst from getting "stuck" on the 1,3-COD oligomers, thus enhancing the catalyst capability for 1,3-COD metathesis and cyclohexene production. The presence of the 1,5-COD units in the polymer should provide other nonconjugated double bonds for the carbenes to coordinate with, increasing the relative amount of digestive metathesis of any polymer products formed. The unconjugated double bonds contributed by 1,5-COD should provide at least one extra site for backbiting which could produce cyclohexene. Metathesis or degradation reactions between the propagating carbenes and the copolymer chains should lead to increased cyclohexene production, depending on which double bond they coordinate with.

We expected an increase in both 1,3-COD consumption and cyclohexene production with the addition of 1,5-COD as a comonomer. As seen in Table 2.6, the disappearance of 1,5-COD was also much slower in copolymerizations with 1,3-COD than in homopolymerizations and no significant increase in cyclohexene production was observed. Cyclohexene production and 1,3-COD consumption for this series of reactions is graphed in Fig. 3.6 and Fig. 3.7. The addition of 1,5-COD as a comonomer did result in an increase in 1,3-COD consumption, but the amount of cyclohexene was still

negligible. Backbiting or the formation of cyclic oligomers to produce cyclohexene was not significantly affected by the presence of 1,5-COD units in the chains or 1,5-COD-derived carbenes. A comparison of the two graphs shows that reactions which were run in parallel using the same batch of catalyst were consistent with respect to 1,3-COD consumption and cyclohexene production. The differences between reactions IV-61 and IV-63 may have been due to the difference in temperature.

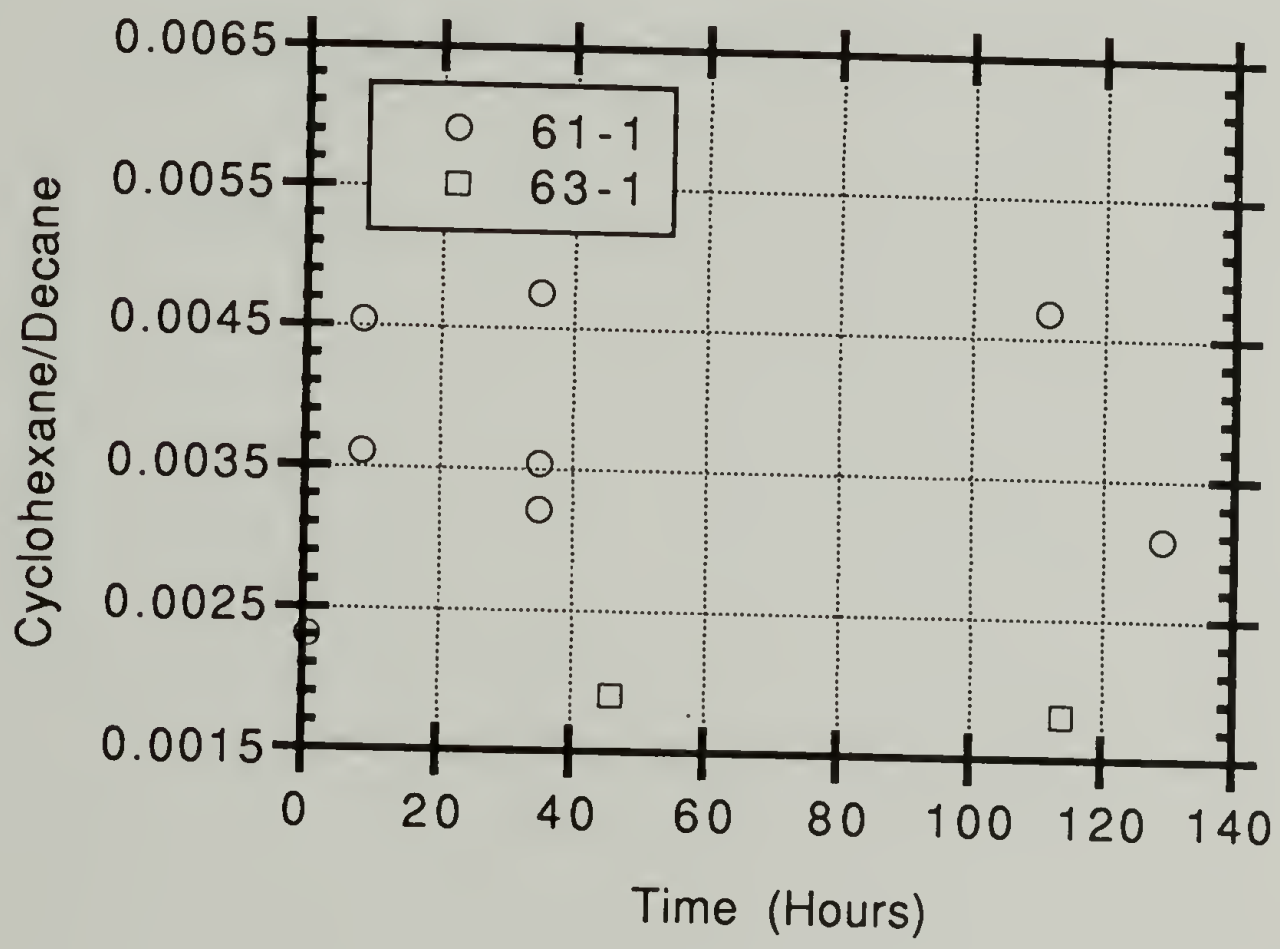
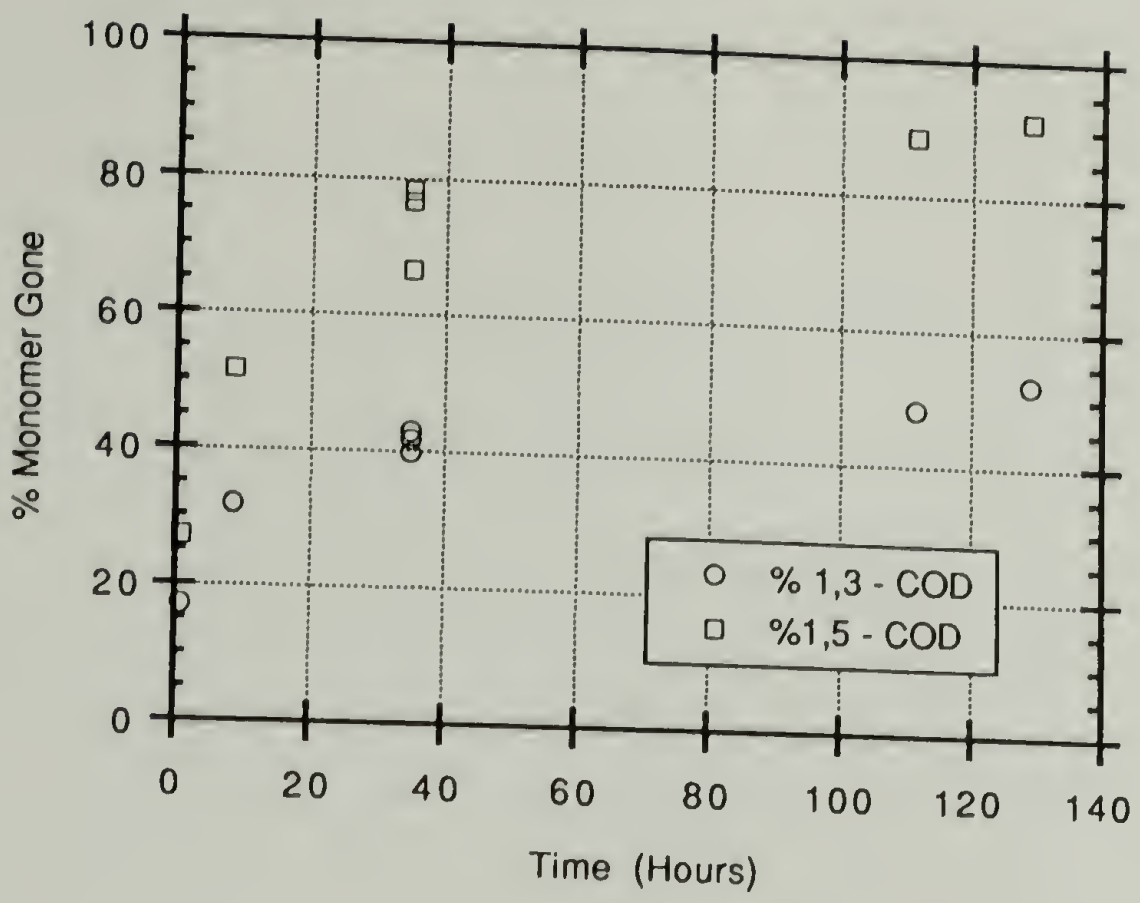


Figure 3.6. Cyclohexene Produced in Type II Copolymerizations of 1,3-COD with 1,5-COD. a) IV-61-1,2 b) IV-63-1,2



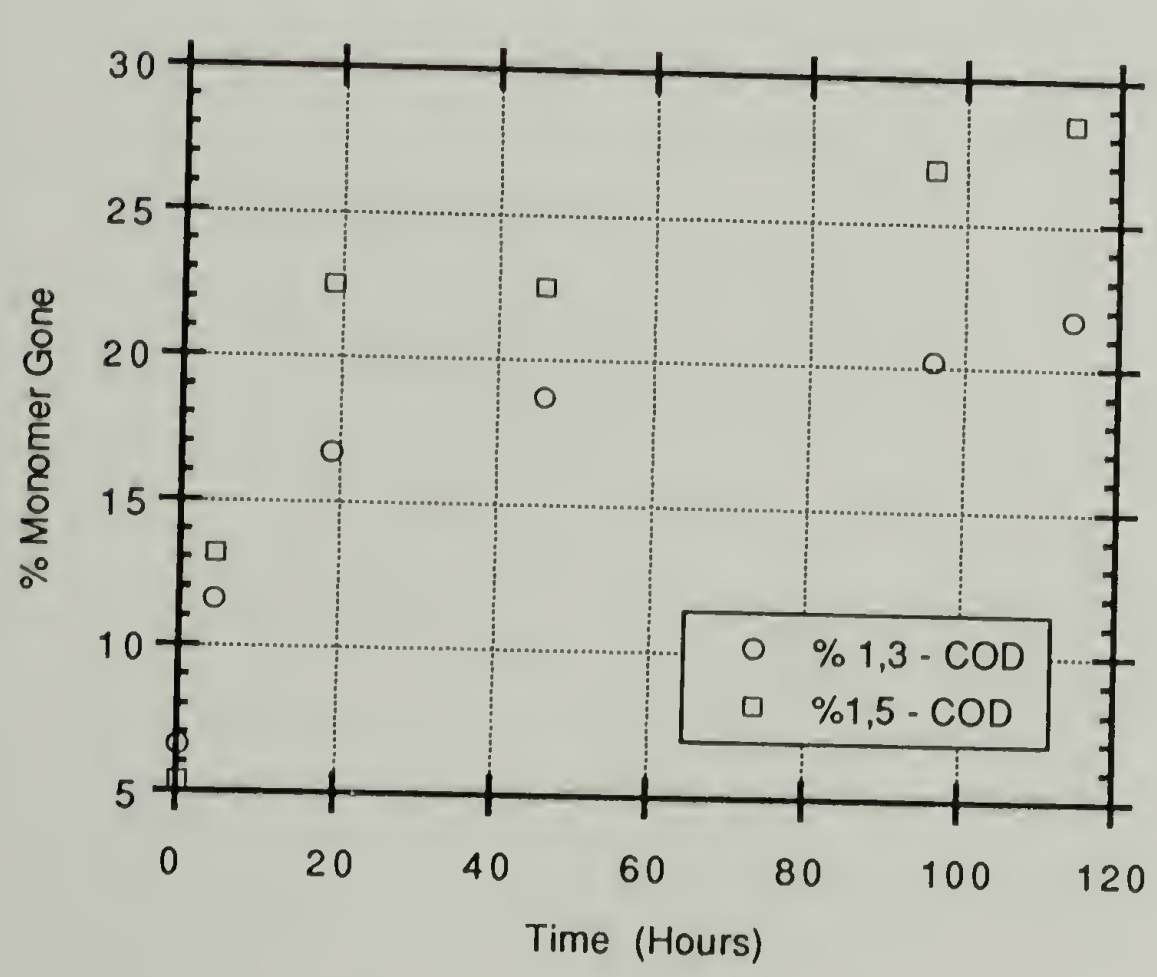


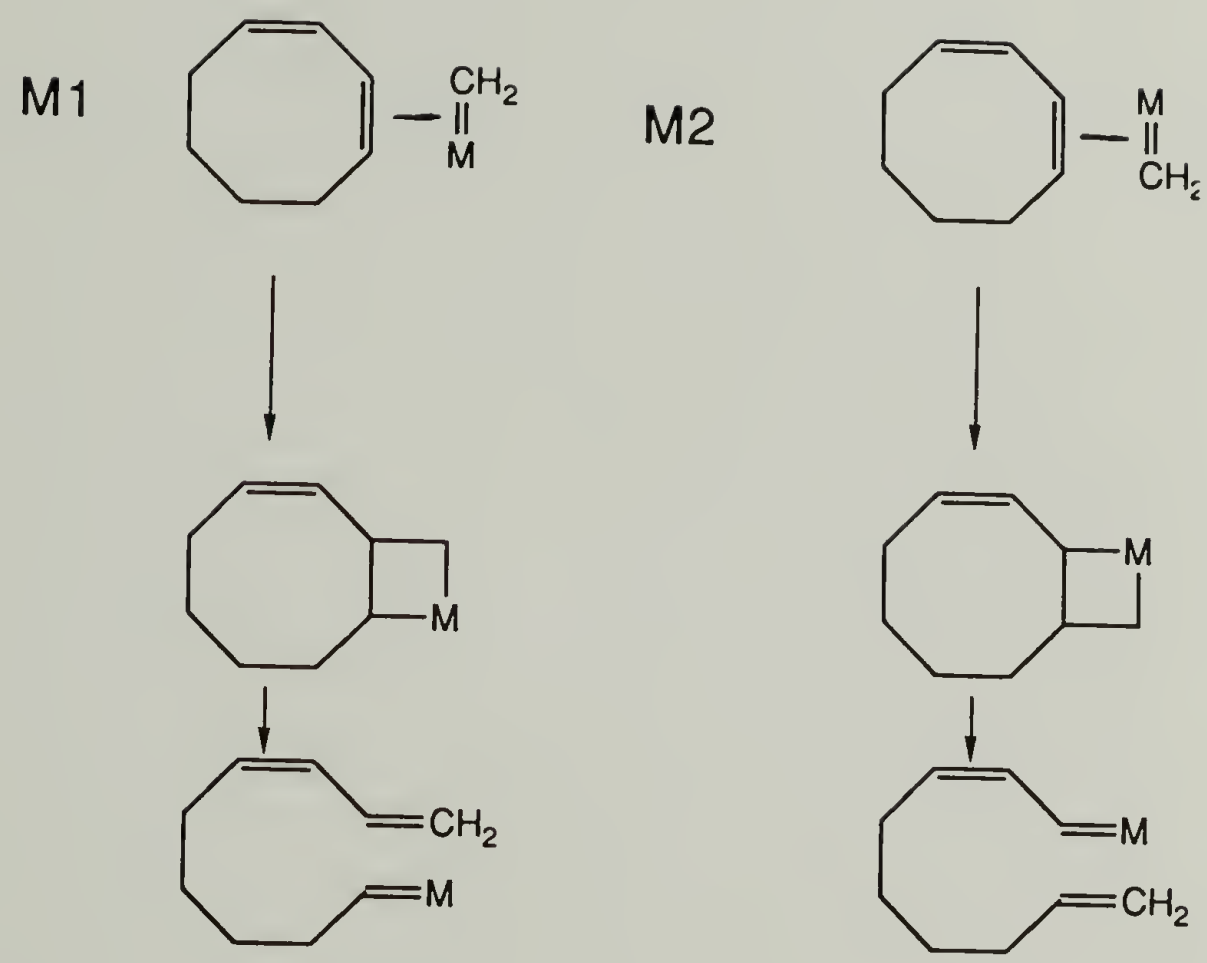
Figure 3.7. Consumption of 1,3-COD and 1,5-COD in Type II Copolymerizations of 1,3-COD with 1,5-COD.a) IV-61-1 b) IV-63-1

Discussion of 1,3-Cyclooctadiene Metathesis Studies

Mechanism for the Formation of Cyclohexene in 1,3-COD Metathesis.

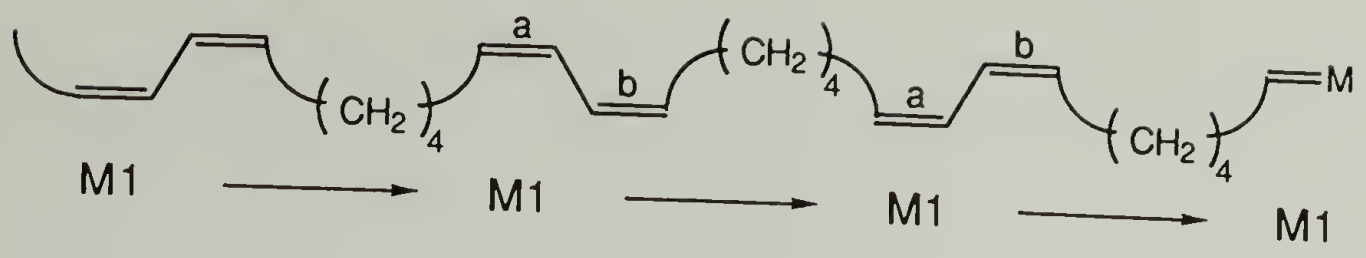
Homopolymerizations of 1,3-COD and copolymerizations with both NBE and 1,5-COD with this catalyst system produced amounts of cyclohexene which fell short of those expected by several orders of magnitude for the complete metathesis degradation of poly(1,3-COD) units. First, we needed to establish whether polymer formation was occurring by a metathesis mechanism in the first place. If 1,3-COD and $WCl_6/SnMe_4$ were reacting through a non ring-opening mechanism to consume 1,3-COD, then it would not be surprising that only small amounts of cyclohexene were extruded by backbiting. However, the fact that even a small quantity of cyclohexene was produced indicates that some metathesis products were formed.

As shown in Scheme 3.9, 1,3-COD can be added onto a chain in a head-to-tail (HT), head-to-head (HH) and tail-to-tail (TT) manner to give either an M1 or an M2 type carbene. A C_8 unit is incorporated in all cases, but the direction of the addition affects the structure of the propagating carbene and the character of the double bond sequences in the chain. The difference between carbene types M1 and M2 is inherited from the structure of the parent metallocyclobutanes formed after coordination of the monomer to the metal center. An M1 type of carbene results from a metallocyclobutane where the tungsten is next to the first carbon of a conjugated complex double bond sequence. An M2 type carbene results if the same double bond complexes from the opposite direction and the metal is next to the second carbon of the conjugated sequence. Metathesis polymerization of 1,3-COD, in the absence of backbiting, could yield several types of products, as shown in Scheme 3.10. Note: The designation of bonds as either *cis*- or *trans*- is arbitrary, because double bond isomerization can occur with this catalyst system during metathesis.



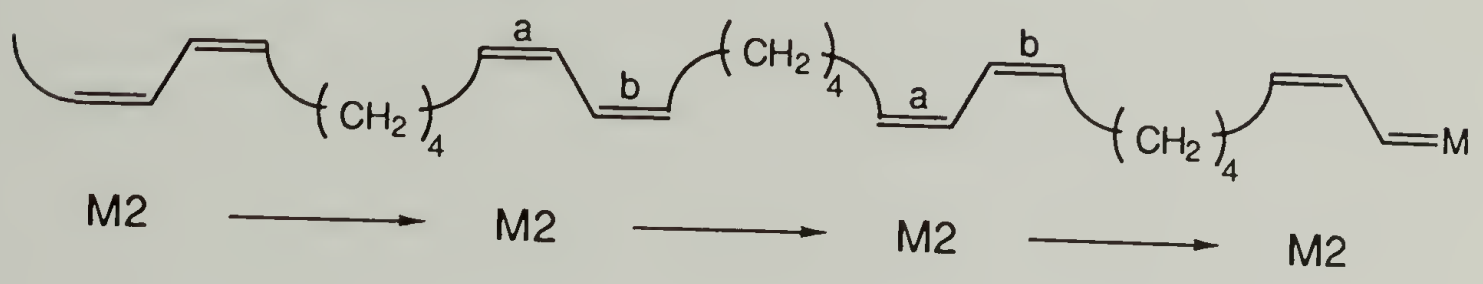
Scheme 3.9. Formation of M1 and M2 Type Carbenes in the Metathesis Polymerization of 1,3-COD.

M1 Followed by M1



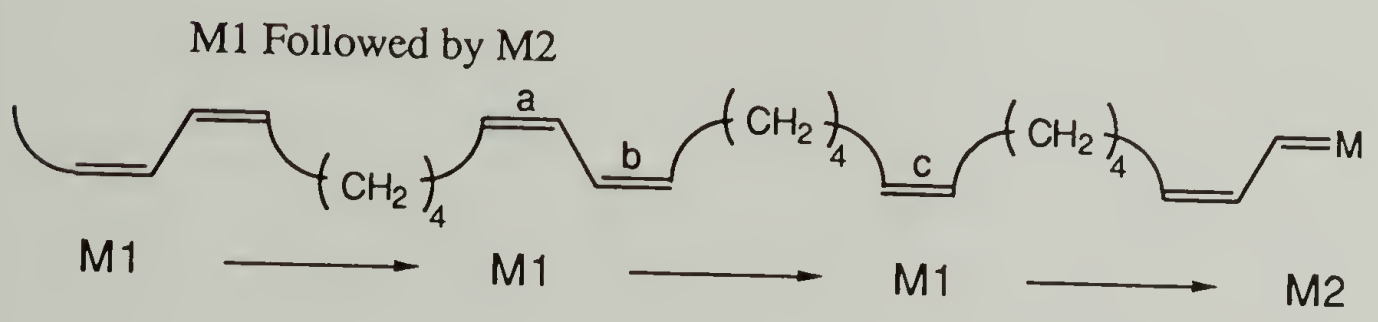
1

M2 Followed by M2



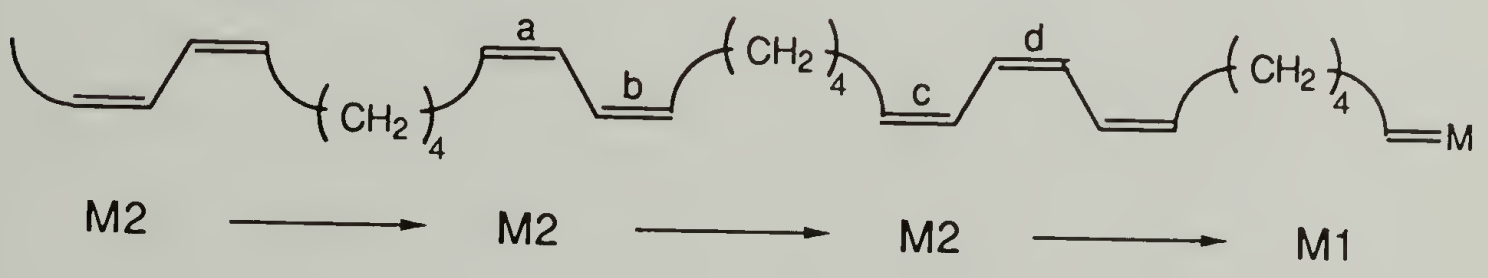
2

M1 Followed by M2



3

M2 Followed by M1

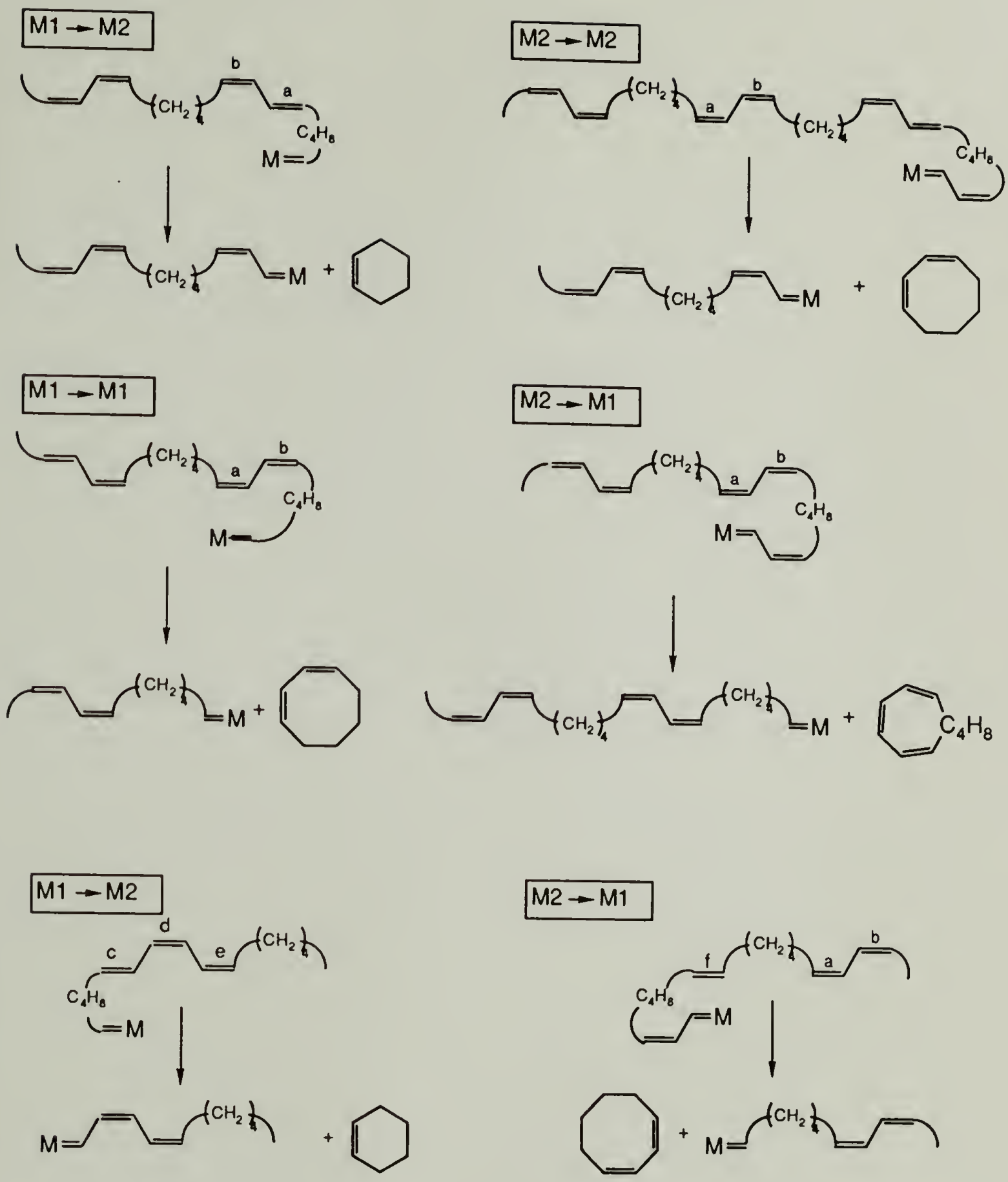


4

Scheme 3.10. Polymer Chains Resulting from Different Combinations of M1 and M2 Type Additions in the Metathesis of 1,3-COD.

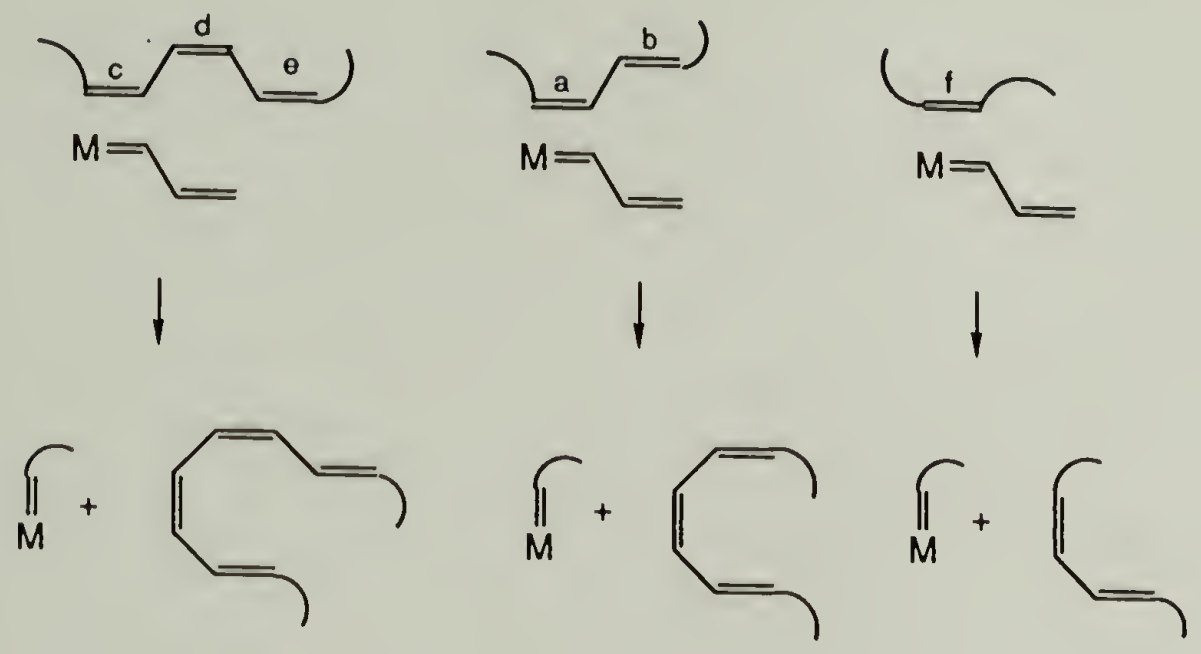
As shown in Scheme 3.11, cyclohexene can be extruded from the polymer in several different configurations. If the propagating carbene backbites to the first available double bond in the chain after a series of HT additions, then the products are cyclohexene and an M2 type of carbene. M2 carbenes require a two step backbiting process to produce cyclohexene. The first backbiting reaction produces 1,3-COD and creates an M1 type of carbene which reaches back again to extrude cyclohexene. The third situation arises when an M1 carbene results from a TT addition and it doubles back to coordinate with the double bond labeled C in Scheme 3.11. Other permutations of these events occur when active carbenes react with the double bonds in other neighboring chains.

Not all reactions that lead to a higher degree of conjugation in the polymer chain will produce cyclohexene. As shown in Scheme 3.12, when multiply conjugated carbenes (carbenes with two or more double bonds in conjugation) and sequences of two or more double bonds coordinate to form M1 type complexes, a more highly conjugated chain results, but cyclohexene is not necessarily produced in the process. Scheme 3.12 also shows the mechanisms by which more highly conjugated carbenes are produced. Each carbene moiety has several options. It can add more monomer, it can backbite on itself, or it can coordinate with a double bond on another chain. The probability of any of these options is determined by the relative amounts of monomer, active centers and accessible double bonds in the polymer, as well as their concentration in solution. In dilute solution, the carbene may be more likely to backbite if it has to find its way through a forest of solvent molecules to find monomer. As more catalyst is added to the homopolymerizations, the concentration of active centers increases and the propagating carbenes would be more likely to coordinate with double bonds in the chains than with unreacted monomer.

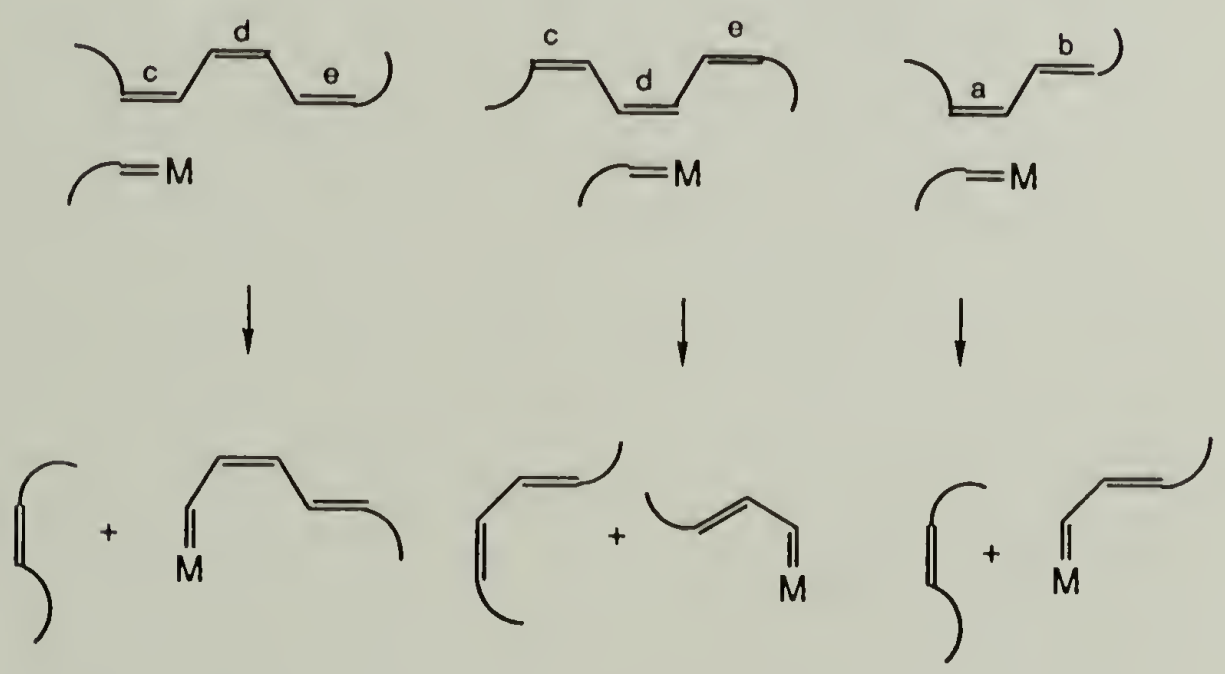


Scheme 3.11. Different Products Formed after the First Backbiting Step in the Metathesis Polymerization of 1,3-COD.

To Increase Chain Conjugation Length: Multiply conjugated carbene complexes in a 1° way



To Increase Carbene Conjugation Length: Carbene complexes in a 2° way



Scheme 3.12.Metathesis Degradation Reactions Yielding an Increased Conjugation Length. a) The Growing Polymer Chain b) The Propagating Carbene

The longest polyenes would be produced by the addition of monomer in a regular HT manner until all of the 1,3-COD had been polymerized, followed by degradation of the resulting polymers by backbiting. Likewise, the situation which would produce the maximum amount of cyclohexene would be one where a head-tail product was slowly digested by the backbiting mechanisms described above, one of which involves the regeneration of the starting material. Ultimately, one would like to be able to convert large amounts of 1,3-COD to polymer and then adjust reaction conditions to promote polymer degradation reactions. This would allow better control of the molecular weights of the starting homopolymers and hopefully of the product polyenes.

Formation Cyclohexene vs. Polyacetylene. When we ran these experiments, we used the quantities of cyclohexene produced to measure the conversion to PA; this may not have been the best indication of degradation progress. As shown in Scheme 3.11, PA can be one of the by-products of carbene-chain interactions, and equimolar amounts of cyclohexene are not necessarily produced. The amounts of cyclohexene do not necessarily correspond to the degree of conversion to PA. The PA-like structure can result from both "immediate backbiting" and from interchain metathesis reactions which would produce carbene-oligomer segments. Ideally, we could expect to see equal moles of cyclohexene and PA from the poly(1,3-COD) if the monomer had polymerized in a regular head-tail fashion. However, degradation of homopolymers of 1,3-COD containing HH, HT, TH and TT combinations could require more intermolecular reactions between chains, as opposed to the direct formation of cyclic oligomers. Streck reports that 1,4-COD polymerizes in a strict HT fashion to give a perfectly alternating copoly(propene-penten)amer, and he attributes the regularity of the product to the presence of small amounts of 1,3-COD (0.6%) present as an impurity.[52] We cannot be sure that 1,3-COD homopolymerizations will behave in the same manner. A mixture of products (HH, HT etc.) may make it impossible to achieve the balance between intramolecular and

intermolecular metathesis reactions necessary for complete decomposition of poly(1,3-COD) into polyacetylene and cyclohexene. As a result, we might see amounts of cyclohexene which were less than the equimolar quantities expected under ideal conditions. However, we would not expect our results to be several orders of magnitude off. Using the $WCl_6/EtAlCl_2$ catalyst system, Hocks et. al. recovered close to the theoretical yield of cyclohexene from the intramolecular disproportionation of cis, trans-cyclodeca-1,5-diene.[53] Based on his results, it was reasonable to have expected equimolar quantities of cyclohexene and acetylene units.

Another explanation for the small amounts of cyclohexene produced may be that it is produced, but under not detected under reaction conditions. Most of the reactions were run at 75°C to increase the solubility of the PA portion of the product and avoid the solubility problems encountered in the DCCB polymerizations. In those reactions, the insolubility imposed on the polymer by the extended conjugation may have forced the propagating carbene out of solution. Cyclohexene boils at 83°C, and evaporation could have added uncertainty to the measurements. We could argue that all of the cyclohexene formed would have boiled away, but this this is not probable for several reasons. First, although the oil baths were at 75°C, the reaction mixtures themselves were probably at least 10°C below the cyclohexene boiling point. In addition, the reactions were run in tubes sealed by teflon stopcocks, and other than being sampled very quickly by cannula, the reactions were not open to the atmosphere. Despite the long duration of some of the reactions, at least a portion of any cyclohexene produced must still have been present. More importantly, the second set of copolymerizations with 1,5-COD were run at room temperature, and although there is a lot of scatter in the data, cyclohexene production did not increase significantly. The results from the 1,5-COD copolymerizations (IV-63) indicate that polymerizations at lower temperatures would not have made up the difference between the amounts of cyclohexene observed and the equimolar amounts of cyclohexene

and PA expected. Running the reactions at 75°C may have taken the quantitative edge off of our results, but should not have affected their qualitative value.

Our data indicates that the polymer obtained by the interaction of 1,3-COD with $WCl_6/SnMe_4$ cannot be degraded by backbiting mechanisms, under reaction conditions. This naturally leads us to question those reaction conditions. The $WCl_6/SnMe_4$ system came highly recommended both for the metathesis of internal olefins and for the metathesis degradation of hydrocarbon polymers. Degradation studies of polybutadiene[54] and isoprene as well as several other unsaturated hydrocarbon polymers and networks have been reported, using this system. The $WCl_6/SnMe_4$ catalyst system has a solid reputation for long life and freedom from side reactions for intermolecular degradation reactions and for the polymerization of internal olefins.[55-56]

We used a well established ratio of catalyst to cocatalyst in these experiments of $WCl_6/SnMe_4$ = 1/2. This ratio had proved successful in previous metathesis studies in our research group using NBE, 1,5-COD and several other cyclic olefins. There was no reason to expect that polymerizations with 1,3-COD would require a different combination of catalyst and cocatalyst.

The initial monomer to catalyst ratios used in these studies were fairly concentrated, ranging from 30/1 to 72/1. Higher concentrations than 50/1 have reportedly produced cationic side products using WCl_6 with aluminium cocatalysts. Hocks reported that a ratio of 37/1 mono to WCl_6, $EtAlCl_2$ gives cationic oligomers as well as cyclohexene alkylation products.[5758] This is not commonly seen with the $WCl_6/SnMe_4$ system, although these types of side reactions certainly could have played a part. The homopolymerizations where additional aliquots of catalyst were added had very high concentrations of catalyst. These conditions may have led to increased side reactions either with the unsaturated polymers formed or with free monomer. Cationic side

reactions would decrease the number of coordination sites for backbiting and intermolecular metathesis, and hence the amount of cyclohexene seen. Other groups also found that adding fresh catalyst at intervals was required for complete degradation.[59,60] A more positive consequence of the high monomer/catalyst ratios should have led to the conversion of large amounts of 1,3-COD into polymer. The fact that fresh catalyst had to be added and that it was still difficult to achieve significant conversions was surprising.

The elevated temperatures used in these studies may have also led to side reactions, again decreasing the number of coordination sites. However, several of the polymer degradation studies with the $WCl_6/SnMe_4$ system were done at 70-100°C,[5-7,55] so the higher temperatures should not have been problematic. In hindsight, these temperatures may not have been necessary, because the 11-ene oligomer reported by Schrock is soluble in pentane.[61]

There are several ways to interpret the slow disappearance of 1,3-COD and the apparent lack of backbiting reactions to form acetylene oligomers and free cyclohexene.

1) The tungsten carbenes may be unable to coordinate or form metallocyclobutenes with the 1,3-diene units in either the monomer or the polymer, and little productive metathesis results.

2) Both double bonds of the 1,3-dienes are tightly coordinated to the metal and block access to additional monomer or polymer.

The first explanation was quickly eliminated when we considered the slow rate of NBE consumption in copolymerizations with 1,3-COD. Either something was preventing NBE from complexing with the active center, or there were carbene structures present which were slower to metathesize than NBE. In any case, the monomer or the early metathesis products were the most likely candidates for blocking the metal, and so the

problem with monomer conversion to polymer and subsequent formation of oligomers cannot be that these species did not complex effectively with the metal.

Our second explanation accounts for many of the results of these 1,3-COD homo- and copolymerizations. The adjacent double bond in either the monomer or the growing polymer chain may have been such a great ligand that it stayed coordinated to the catalyst. Free monomer and other oligomers could not approach, and the catalyst was deactivated. In essence, 1,3-COD and its oligomers combine with the catalyst to form a stable species and polymerization could not proceed.

There have been other reports of molecules whose structures allow them to complex tightly to the metal, preventing access to the active site and effectively inhibiting polymerization. In the metathesis of pent-2-ene, metathesis is retarded by the presence of terminal olefins which complex more strongly with the metal center than internal olefins. Several groups have reported that degradation of polybutadiene is difficult and requires repeated doses of catalyst when large numbers of 1,2-units are present.[62-64] With anionic and cationic chain polymerizations, transition of the propagating chain end to a more stable type of molecule leads to inhibition of polymerization. Dolgoplosk suggested that in the case of metathesis types of polymerizations, the addition of unsaturated compounds led to more stable carbene complexes and ultimately resulted in the inhibition of further polymerization.[65] He used compounds like vinylbutyl ether and vinylbutylsulphide to investigate this concept but by analogy, the reaction of 1,3-COD with $WCl_6/SnMe_4$ could have resulted in a more stable carbene complex that could not coordinate additional monomer.

Work by McCarthy and Patton showed that the rate of polymerization is dependent on the reactivity of the propagating carbene, as opposed to the ring strain inherent to the monomer.[21] The reactivity of some common monomers for metathesis decreases in the

order NBE>Cyclopentene>COE~1,5-COD, as a result of their carbene structures. Due to steric constraints between the growing polymer chain and the metal center, the NBE carbene exists in the unrelaxed or decoordinated state after it has metathesized an olefin. It cannot keep the newest double bond coordinated, resulting in higher propagation rates because there is an empty coordination site for monomers to approach the metal center, and coordinate. Carbenes derived from 1,5-COD and COE are more likely to exist in the unrelaxed state, because the last double bond can remain coordinated to the metal. They are typically not as reactive as NBE derivatives because in their case, there is always a second double bond in the immediate coordination sphere of the metal.

Small amounts of 1,3-COD are reported to increase the *cis* content of polymers prepared from several different monomers.[66] In general, higher *cis* content is an indication of a sterically hindered carbene, which restricts monomer access to a specific configuration. Large amounts of 1,3-COD had negative effects on the yield. When only small amounts are present, one equivalent of 1,3-COD must complex with the metal and restrict the access of the other monomer. A similar effect was reported for *endo*-dicyclopentadiene. It can act as a permanent ligand because of its potential to chelate in a bidentate fashion. Polymerization with $RuCl_3 \cdot 3H_2O$ resulted in a polymer with high *cis* content.[67] Streck took advantage of the stereoregularity influence of 1,3-COD to make COE and 1,5-COD block copolymers in which the COD block was *cis*-enriched and formed a softer segment than the COE block.[66] He also noted that 1,3-COD inhibition was negligible with 1,5-COD and NBE, but greater with COE and cyclodecatriene.

Since these studies have been completed, Grubbs has reported the polymerization of cyclooctatetraene (COT), using the alkylidene catalysts developed in his laboratory.[68] Clearly, the presence of conjugated double bonds is not a universal metathesis inhibitor; he obtained shiny silver polyacetylene films from these reactions. Solid state polymerization using neat COT and films of evaporated catalyst solution gave smooth

films of poly(COT), whereas in dilute solution, he saw extensive backbiting to produce benzene. The polyacetylene that resulted from the latter reactions fell out of solution in the form of a black powder. Grubbs refers to these backbiting reactions as "cycloextrusion." According to Grubbs, in dilute solution the conjugated sequences of double bonds were insoluble and precipitated out of solution before they had a chance to become entangled with other chains and obtain any mechanical integrity. When he ran these same solution experiments in NMR tubes and spun them during the polymerization, the sides of the tubes were coated with a lustrous silver coating which he explained as polyacetylene chains which had been compressed together and entangled by centrifugal force.

The work by Grubbs showed that these sort of backbiting reactions can be major players in the metathesis of cyclooctatetraene. Unless polymerizations were done with COT as the solvent, he saw substantial quantities of benzene and significant morphological changes in the product polyacetylenes. This was inconvenient in his case, whereas we tried to encourage the formation of cyclic oligomers. We did not look for benzene in our reactions, but carbenes attached to extensively conjugated chains might have produced benzene through backbiting.

Conclusions

Several different experiments would be required in order for us to understand what could be happening between 1,3-COD and the $WCl_6/SnMe_4$ catalyst system. Monitoring the amount of cyclohexene produced over time may not have been adequate to determine the proportion of cyclic oligomers formed. Simultaneous characterization of these products by NMR and IR would be helpful in determining the structure and distribution of the conjugated systems. We need to explore different ways to control the formation of cyclic oligomers such that the product retains sufficient mechanical integrity. Copolymerization might be one way to accomplish this, but other catalyst systems are also

an option. Grubbs' work showed that cycloextrusion is possible, and the alkylidene catalyst he used would be a promising alternative to the $WCl_6/SnMe_4$ system that we employed in the studies described above. Apparently the conjugated bonds in the polymer did not inhibit the metathesis activity of this catalyst.

The solid state reactions would make homopolymers which could then be redissolved to encourage the backbiting reactions which would produce polyacetylene and cyclohexene. By making the homopolymers first, it would be easier to control molecular weights and their distribution. The addition of chain transfer agents and other monomers could be used to tailor solubility and tractability of the products, both in the neat polymerizations and in the subsequent oligomerization reactions.

The combination of 1,3-COD and the $WCl_6/SnMe_4$ catalyst system was less than ideal in these studies for producing latent conducting polymers. More accurate conditions for monitoring the polymerization by GC and better product analysis may have led to different or more definitive conclusions about the interactions between 1,3-COD, the catalyst and the initial metathesis products, but the bottom line would have remained the same. The amounts of cyclohexene seen in these studies were negligible, and the combination of this catalyst system with this monomer will never be a viable route to polyacetylene. However, this study does illustrate some of the unique aspects of the metathesis reaction. In designing materials with extensive conjugation, one cannot ignore a polymerization reaction that places double bonds directly in the main chain.

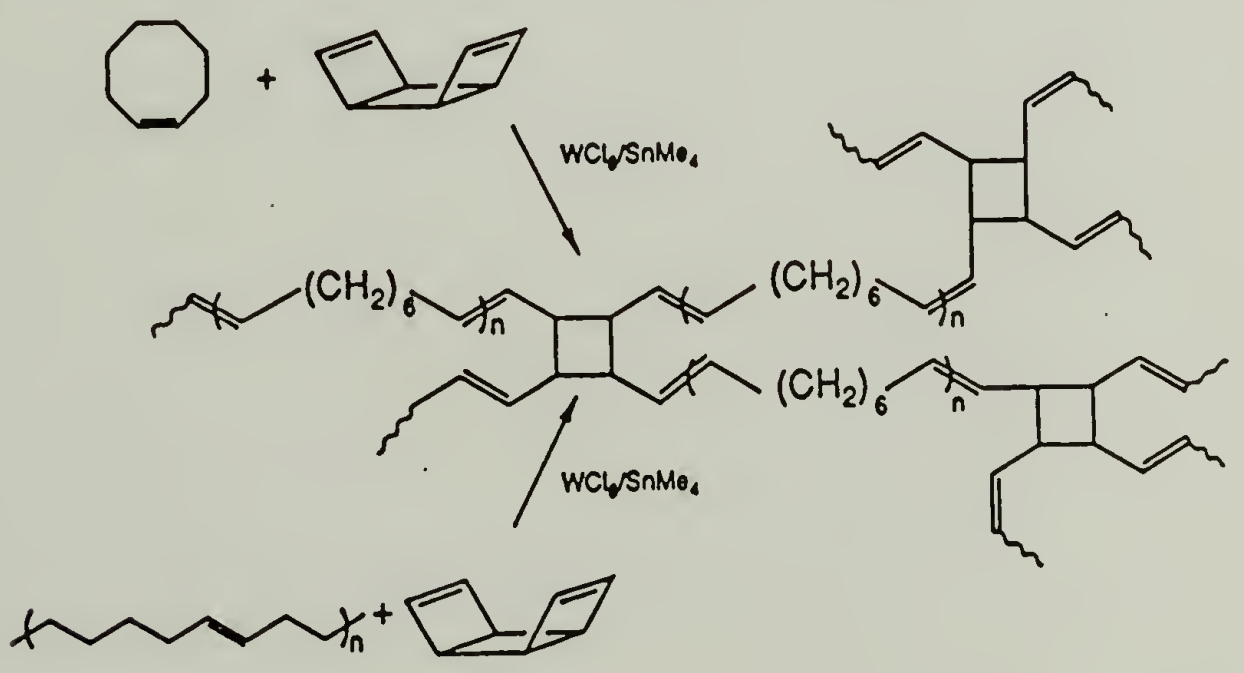
syn-Tricyclo[4.2.0.0^{2,5}]octa-3,7-diene: A Metathesis Crosslinking Agent

Solution Homopolymerization Studies

Syn-tricyclo[4.2.0.0^{2,5}]octa-3,7-diene (TCOD) was synthesized using procedures reported by Paquette[69] and Avram[70] in 30% yield to give 3.1 g of the crosslinking agent. Homopolymerization of TCOD using the $WCl_6/SnMe_4$ catalyst system produced an insoluble polymer immediately after the introduction of TCOD to the catalyst mixture. The reaction mixture solidified completely after the addition of TCOD. Clearly, TCOD was susceptible to polymerization using this metathesis catalyst; the copolymerization studies described below were conducted to characterize its behavior as a crosslinking agent.

Solution Copolymerization Studies

Copolymerizations with cyclooctene (COE) using the $WCl_6/SnMe_4$ catalyst system were carried out by two different methods, as shown in Scheme 3.13. In the top scheme, polymerization was initiated by adding a solution of WCl_6 to a mixture of $SnMe_4$, COE and TCOD. In the bottom scheme, a solution of the crosslinking agent is added to a polymerization which is already in progress. COE homopolymerizations were run as



Scheme 3.13. Copolymerization of TCOD with COE by Two Different Routes with $WCl_6/SnMe_4$

control reactions to observe catalyst activity in the absence of TCOD. In the first type of copolymerization, the control reaction remained a red brown color for at least one hour, before turning the greenish brown color, usually indicative of an inactive catalyst. The reaction mixture which contained TCOD in a ratio of 20/1 (COE/TCOD) turned a greyish-blue metallic color immediately upon addition of WCl_6. Analysis by GC showed that all of the TCOD had been consumed, within the limits of GC detection. Heptane and TCOD were initially present in similar quantities and the ratio of heptane to nonane (a second internal standard) remained constant before and after addition of the WCl_6 solution. Typically 20% of the cyclooctene disappeared from the tube which contained the crosslinking agent, as compared to 40% in the control reaction. NMR analysis of the products of these copolymerizations after isolation by precipitation in methanol showed the expected signals for poly(COE). In addition, peaks at 41.2 ppm in the ^{13}C spectrum and 3.5 ppm in the ^{1}H spectrum represent the carbons and protons, respectively, from the cyclobutane ring of TCOD (see Figure 3.8 and Figure 3.9). There are no peaks in the 5.8-7.0 ppm region of the ^{1}H spectrum, where we would expect to find signals due to the olefinic protons of any unopened cyclobutene rings, indicating that both cyclobutene rings had opened.

In the second type of copolymerization experiment, the crosslinking agent was added to a COE polymerization which was in progress. A homopolymerization of COE was run in parallel as a control. After 20 min, 47% of the COE had been digested by the catalyst. TCOD (0.015 mmol) was added to give a product with 100 COE units between crosslinks, based on the amount of monomer already consumed. The sample began to gel immediately and formed a solid, gelatinous precipitate within 15 min. Dilution in chlorobenzene allowed sampling for GC and it was determined that 88% of the COE had been consumed by the end of the reaction, resulting in an actual ratio of COE/TCOD of 320/1 and a crosslink density of 160 units between junction points. As in the previous

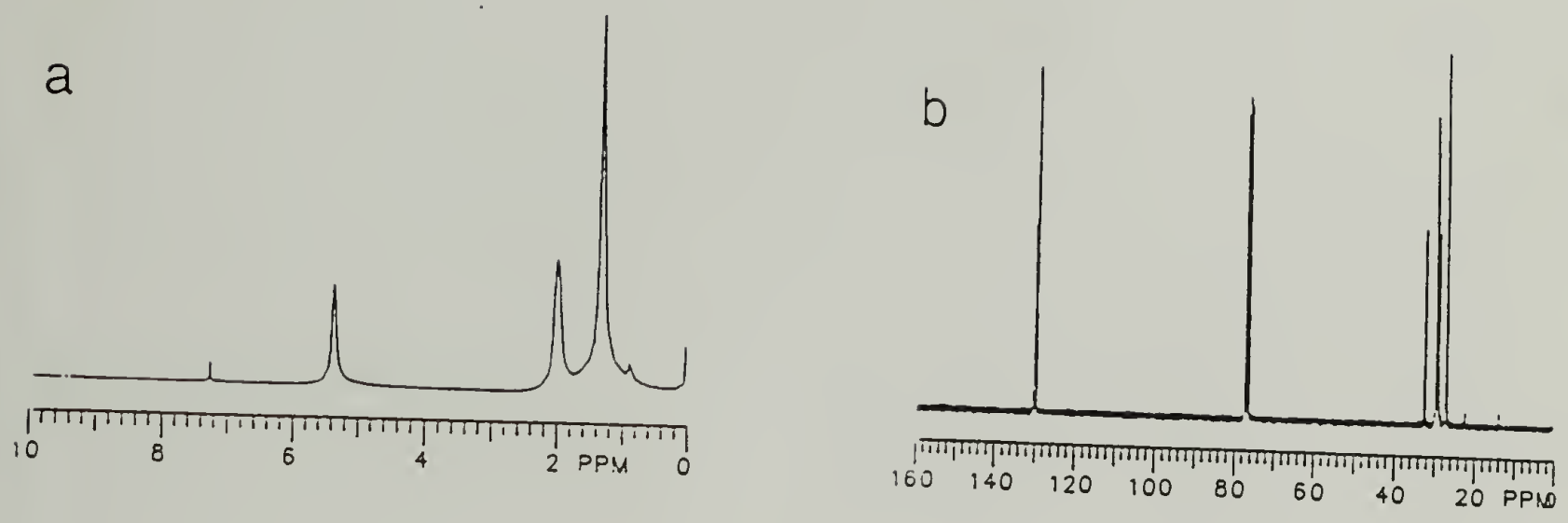


Figure 3.8. ^{1}H-NMR (a) and ^{13}C NMR (b) Spectra of poly(COE).

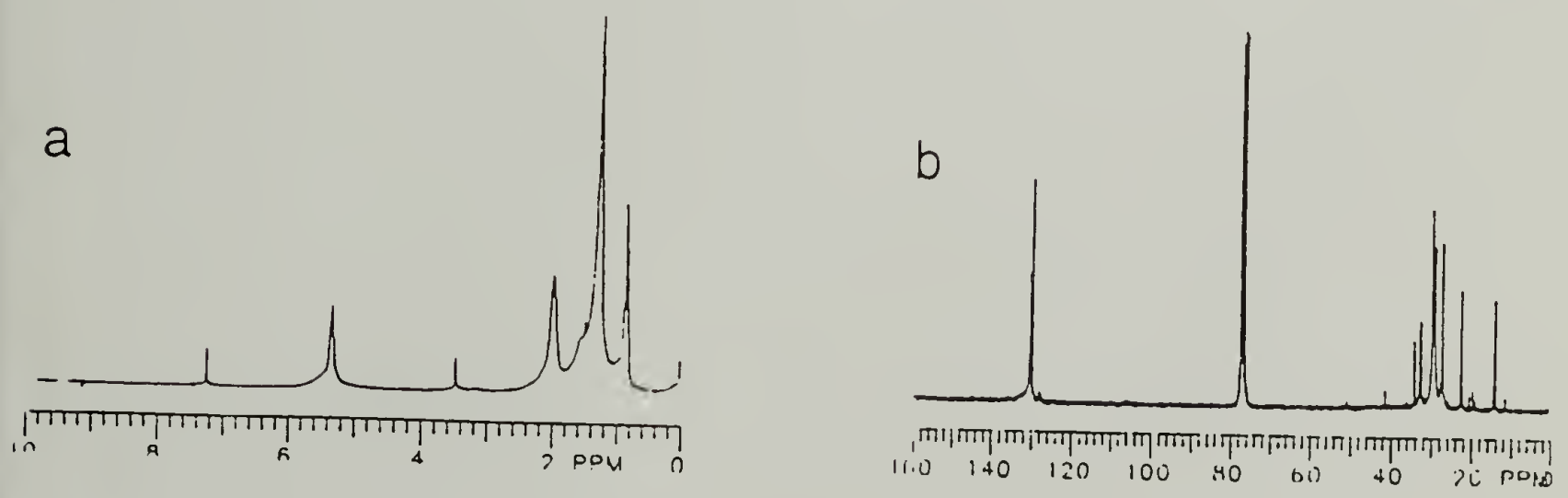


Figure 3.9 ^{1}H-NMR (a) and ^{13}C NMR (b) Spectra of poly(COE-co-TCOD).

copolymerization experiments, no TCOD was seen in the GC, although the heptane used as an internal standard was clearly present. In the control reaction, 89% of the COE had reacted. Some of the gel was dried on the vacuum line, swollen in $CDCl_3$ and analyzed by NMR, but no resonances attributable to cyclobutane were observed, due to the low concentration of crosslinking molecules. The disappearance of the peaks representing TCOD on the GC trace and in the NMR spectra indicated that at least one of the cyclobutene rings had opened and that cyclobutane rings had been incorporated into the polymer. We saw no evidence of unopened cyclobutene rings. The viscosity changes in this second set of copolymerizations convinced us that crosslinking had indeed occurred.

We repeated the copolymerization experiment described with the addition *cis*-2-hexene as a chain transfer agent. This kept viscosities low to facilitate GC sampling and allowed us to measure differences in the product molecular weights and distributions by GPC. A comparison of the largest peaks present in the GPC traces in Fig. 2.5 show that there is a difference between the sample which contained crosslinking agent and the one which did not. As we would expect, the molecular weight of the crosslinked sample was higher with respect to a polystyrene calibration and the distribution was broader, because low molecular weight fragments have been joined together by the crosslinking agent. Unfortunately, heterogeneities in all of the precipitated reaction products from this set of experiments resulted in poor quality GPC data. There were small clumps of gray solid as well as low molecular weight oils and GPC of these materials proved difficult, possibly due to water contamination of the samples. This quick and dirty GPC analysis did show however that the differences between the crosslinked and non-crosslinked samples were not as dramatic as we had hoped. GPC was not the ideal way to characterize the differences in these types of polymers because of the wide distribution of configurations possible for the growing chains in the crosslinked products. The nature of the experiment determines that the products will be branched and comparison with

polystyrene molecular weight standards does not account for the elution characteristics of nonlinear species.

Solid Network Samples

Preparation. Other characterization methods were necessary to establish that different concentrations of TCOD in the polymerization mixture would produce networks with different physical characteristics. Properties such as degree of swelling and modulus would be more informative about the effect of different amounts of TCOD incorporated into each sample. Because these samples were crosslinked, a catalyst system was required which would produce samples in a form suitable for testing, without needing to redissolve or reshape them. The WCl_6/Et_2AlCl catalyst system, well known as the Hercules Metton™ catalyst,[71-72] was chosen because it was convenient for the preparation of solid samples. Hercules uses this two component catalyst to produce high modulus and impact strength materials from the polymerization of dicyclopentadiene (DCP) in a Reaction Injection Molding process (RIM). The final product is a partially crosslinked glass; DCP acts as a crosslinking agent by ring-opening at both double bond sites. We chose to polymerize cyclic monomers with a single olefinic bond which would produce samples of a rubber-like consistency, providing a more convenient matrix for testing the effects of an external crosslinking agent. Polymerization trials using NBE (without any TCOD) quickly showed that the fabrication of physically homogeneous samples was not a simple exercise. Norbornene formed foamy, inhomogeneous materials, even when cooled to -20°C immediately after mixing the WCl_6 and Et_2AlCl catalyst components. The melting point of NBE made it difficult to manipulate the monomer solutions without adding more solvent or keeping the transfer pathways heated. The foaming resulted in macroscopic voids in the samples; the exothermic polymerization temperatures may have caused the NBE to boil. This may not have been a problem in the DCP system due to its higher boiling point. Macosko[73] reported homopolymerizations of NBE with the Metton

system, but he used greater concentrations of both catalyst and solvent than would have been appropriate given the mechanical and swelling tests planned for these samples.

Next, we polymerized (COE) and cis-cyclodecene (CDE) with the Metton™ system because they boiled at 145°C and 232°C, respectively and might yield more physically homogeneous, rubber-like materials. Unfortunately, neither monomer formed solid samples in homopolymerization studies with this catalyst. Dall'Asta[74] reported that the polymerization of cyclodecene required low initiation temperatures (-15°C), followed by a slow warming to 70°C after one hour using $WOCl_4$, but these techniques were not effective with the WCl_6/Et_2AlCl system with either monomer. We did find that copolymers in solid form could be prepared from both CDE and COE by mixing NBE with one component of the catalyst and either CDE or COE with the other. COE was chosen as the comonomer for making the samples for physical characterization because it should have competitive metathesis rates with TCOD, yielding a random network. Despite the advantage of a significantly higher boiling point, the use of CDE introduced the possibility of "crystalline crosslinks" which would lead to inaccurate indications of the molecular weight between crosslinks from our tests.

Several different sample configurations were also investigated. As detailed in the experimental section, the two catalyst/monomer streams were combined in small 10 mL beakers, teflon coated trays and 6 mL culture tubes to form samples in the shapes of plugs, sheets and cylinders, respectively. The samples formed in the culture tubes were the most homogeneous. Those mixed in the trays and in the beakers cured unevenly across the sample, resulting in voids on one side of the sample and unreacted monomer on the other. The success of the polymerizations in the culture tubes may have been due to a faster speed of mixing or more efficient exclusion of oxygen from some of the reactions.

A series of five networks (A-E) was made from equimolar mixtures of COE and NBE, using the monomer to crosslinking agent ratios shown in Table 3.10. A control sample which did not have any TCOD present was prepared under identical conditions and labeled XT. For consistency, a stock solution of NBE and COE was mixed with the different concentrations of TCOD before dividing the monomer mixture into two parts and adding the WCl_6 and Et_2AlCl components. The ratio of WCl_6 and Et_2AlCl to monomer was 1/2000 and 1/300, respectively. The two catalyst components were combined under nitrogen in 6 mL culture tubes to produce small cylinder shaped samples which were relatively void free and of a nice "pencil eraser" consistency, suitable for both swelling and mechanical tests.

Table 3.10. Network Series Synthesis.

Network Name	Millimoles TCOD added	Ratio of Mono/TCOD	Units between crosslinks	M_c
A	1.40	18	9	912
B	0.07	36	18	1823
C	0.28	89	45	4558
D	0.15	166	83	8487
E	0.08	309	155	15804
XT	—	—	—	—

Mechanical tests and swelling studies were carried out on this series of samples to show the effect of crosslinking agent concentration on the physical properties of the copolymer networks. Because the monomer in this case was actually an equimolar mixture of COE and NBE, an average of the molecular weights of each monomer was

used to represent the molecular weight of a single unit. The molecular weight between crosslinks (M_c) and the number of units between crosslinks listed in Table 3.10 were calculated using the ratios of moles of monomer to crosslinker in the feed.

Swelling Test Results. The degree of swelling for an elastomeric network is directly affected by the molecular weight of the chains between crosslinks;[75-7778] we carried out swelling tests on this series of networks to observe the differences between samples with varying amounts of the crosslinking agent. When a linear polymer is immersed in a good solvent, the material swells and the solvated chains are forced apart until all the chains have been have been freed of entanglements and the polymer is in solution. With a network, these chains cannot be completely separated and equilibrium is reached in the swollen state when the elastic restorative forces of the network are exactly balanced by the forces of dilution. The effective molecular weight between crosslinks, the polymer-solvent interaction parameter and the temperature act together to control the degree of swelling which characterizes this equilibrium. We can use a derivation of the Flory-Huggins equation to express this equilibrium in terms of the volume fraction of swollen polymer,which can be rearranged to calculate M_c, as shown in Scheme 3.14

$$0 = RT\left[\ln(1-\varphi_2) + \varphi_2 + \chi_1\varphi_2^2 + V_1(\rho_2/M_c)(\varphi_2^{1/3} - \tfrac{1}{2}\varphi_2)\right]$$

$$\frac{-\rho_2}{M_c} = \frac{\ln(1-\varphi_2) + \varphi_2 + \chi_1\varphi_2^2}{V_1(\varphi_2^{1/3} - \frac{1}{2}\varphi_2)} \text{ moles cm}^{-3}$$

M_c = Average Molecular Weight Between Crosslinks

V_1 = Molar Volume of the System

χ_1 = Polymer-Solvent Interaction Parameter

ρ_2/M_c = Crosslink Density (moles cm^{-3})

Scheme 3.14. Calculation of M_c using the Flory Huggins Equation.

Samples from each network composition were swollen for three days in toluene and the changes in weight and diameter were recorded. The weights obtained from these studies were used to calculate the molecular weight between crosslinks, using the equations in Scheme 3.14. The calculations were carried out using polymer densities ranging from 0.90g/ml to 1.1g/mL in combination with polymer-solvent interaction parameters (χ) equal to 0.45 to 0.50. The complete set of results from these calculations can be found in Notebook VI. The values shown below in Table 3.11 assume a polymer density of 0.95g/ml and a χ parameter of 0.45, which are typical numbers for polybutadiene and natural type rubbers.[79] Even the lightly crosslinked samples indicate relatively low molecular weights between crosslinks and the calculated values for the most and least crosslinked samples differ only by a factor of two and half.

The ratio of the final weights or dimensions divided by the initial ones for the series is listed in Tables 3.12, 3.13, 3.14 and plotted in Figures. 3.10 and 3.11. As expected, the plots show a gradual increase in the amount of swelling with decreased amounts of TCOD, with a distinct difference between the samples containing TCOD (A-E) and the control samples with no crosslinking agent added (XT).

Table 3.11. M_c Calculated using the Flory-Huggins Equation. (∂=.95 X=.45)

Sample	Mc Theoretical	Swell 74	Swell 93
A	912	805	439
B	1823	632	518
C	4558	815	930
D	8487	648	694
E	15804	1093	1039
XT		4573	1920
A Dry	912	1243	
XT Dry		9098	

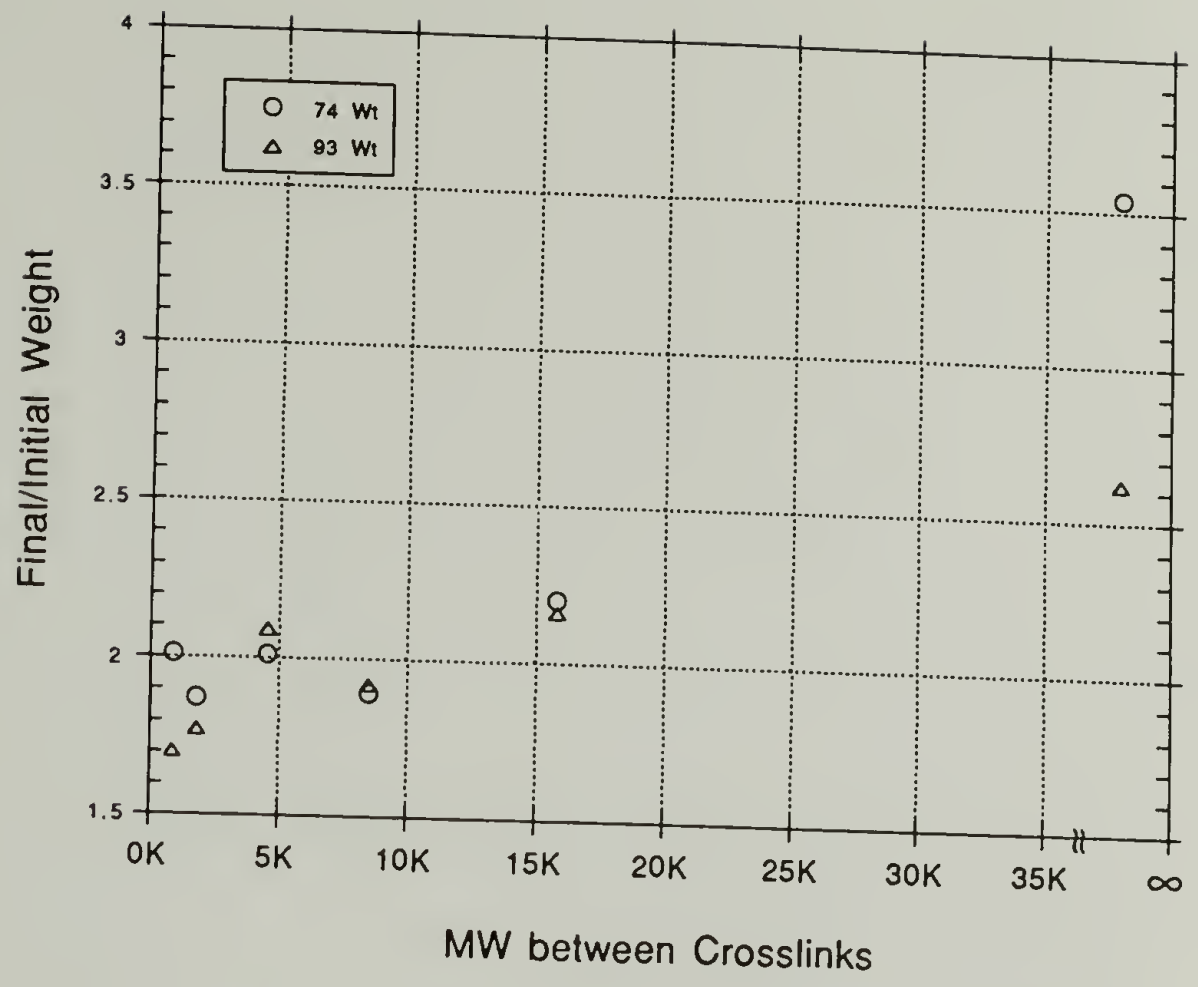


Figure 3.10. Swelling (Final/Initial) Weight vs M_c.(V-74, 93)

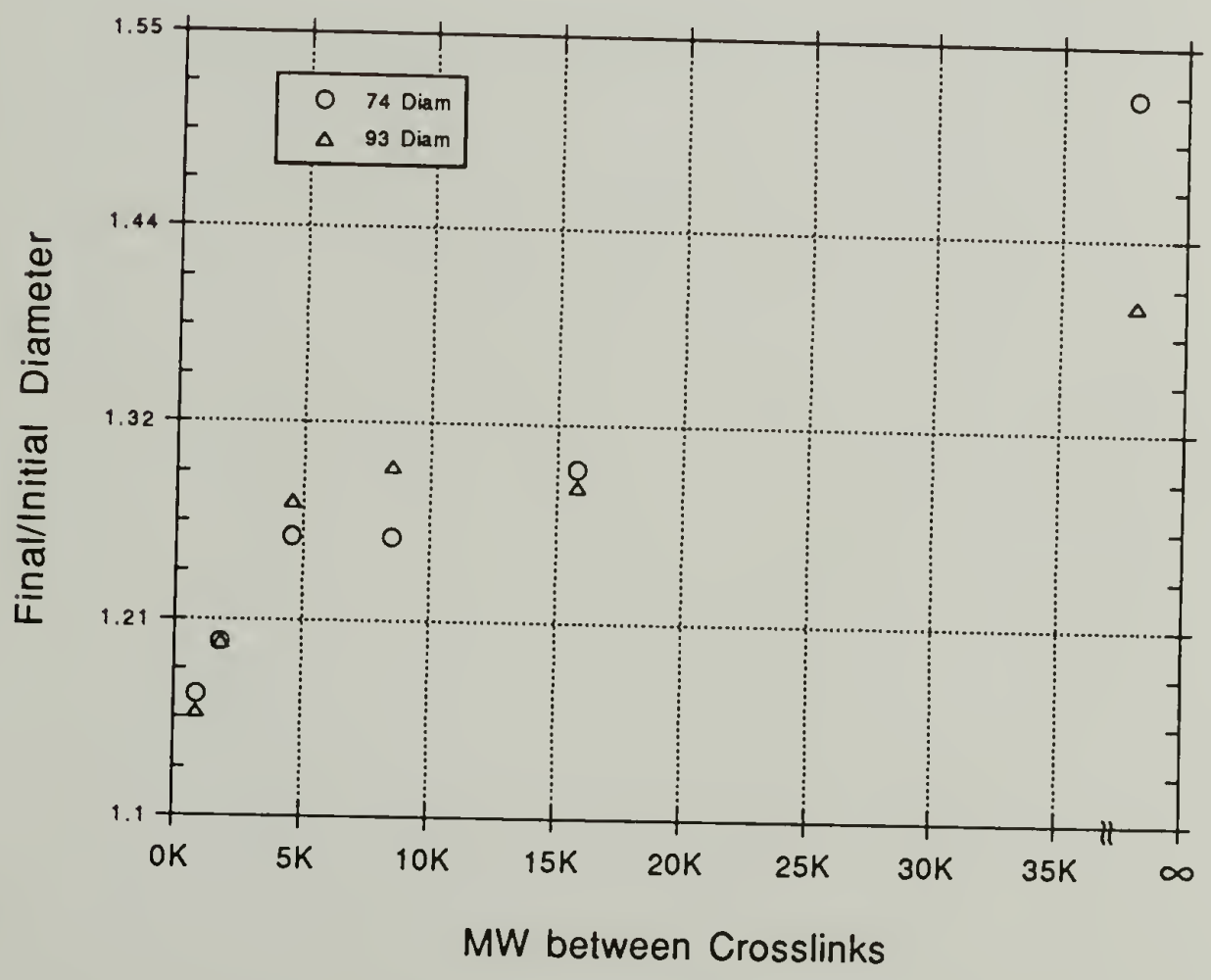


Figure 3.11. Swelling (Final/Initial) Diameter vs M_c. (V-74, 93)

Table 3.12. Degree of Swelling (Final/Initial) for V-74.

Sample	Final/Initial		Final/Initial (2 Days Later)	
	Diameter	Weight	Weight	Weight
74 A	1.17	2.01	1.98	1.97
74 B	1.20	1.87	1.84	1.89
74 C	1.26	2.01	2.00	2.03
74 D	1.26	1.89	1.84	1.88
74 E	1.30	2.20	2.26	2.16
74 XT	1.52	3.54	3.37	3.50

Table 3.13. Degree of Swelling (Final/Initial) for V-93.

	Final/Initial	
Sample	Diameter	Weight
93 A	1.16	1.70
93 B	1.20	1.77
93 C	1.28	2.09
93 D	1.30	1.92
93 E	1.29	2.16
93 XT	1.40	2.62
92 dry A	1.29	2.29
92 dry XT	1.72	4.57

Table 3.14. Degree of Swelling (Final/Initial) for Network Sample B.;

	Final/Initial	
Sample	Diameter	Weight
B 1	1.23	1.69
B 2	1.18	1.59
B 3	1.17	1.61
B 4	1.20	1.64
B 5	1.19	1.89
B 6	1.17	2.02
Average	1.19	1.74
Standard Deviation	0.02	0.17

In order to obtain a more accurate figure for the initial dry weight, some samples of Network A and of the control network were placed under vacuum at 50°C to remove residual solvent, monomer or other plasticizers which might have been present. As shown in Table 3.13, these "dry" samples swelled more than those which were swollen directly after polymerization, indicating that the swelling ratios shown in the tables may not be accurate with regard to the absolute amount of swelling. However, the trends showing that the more highly crosslinked networks swell to a lesser degree should still be valid.

To find out more about the structure of the final polymerization products, the swelling effluent from the second set of swelling experiments was analyzed to determine the types of materials extracted and their concentrations. As shown in Table 3.15, the concentration of COE per gram of sample was relatively constant for the series after the concentration of COE in each vial of swelling effluent was normalized by the original

weight of the sample. If the concentration of unreacted COE was the same for all the samples, and there were no indications of residual NBE or TCOD, then the degree of polymerization should be similar for all the networks in the series. In reaching this conclusion, we assume that both samples for each TCOD concentrations are homogeneous with respect to the degree of polymerization and that our calculation is valid despite the fact that the initial weights include the residual monomer in question, plus the reaction solvent and other additives.

A similar analysis of an entire polymerization sample of Network B was used to determine the total concentration of residual monomer in that network composition and is shown in Table 3.16. Based on the moles of monomer originally present, the degree of polymerization was calculated to be 81%. The samples from network B were also used to check our assumption above that the degree of polymerization was constant throughout a whole sample. A standard deviation of 0.154 between the normalized values for the B series (Table 3.17). shows that this was a reasonable assumption.

In order to get the most accurate information about network dimensions, all residual monomer and unattached polymer chains which are not covalently bound to the network should be extracted. The networks should then be redried before obtaining initial and swollen weights for the networks. Unattached polymer in the networks takes up space which might be occupied by solvent molecules and leads to discrepancies between the weight and volume measurements used to determine the degree of swelling.

Despite the variables discussed above which could contribute a measure of inaccuracy to the calculation of M_c, these swelling measurements clearly show that the samples are more highly crosslinked than the initial stoichiometries led us to expect. The calculated values indicate that TCOD is not the only source of crosslinks in this system.

Mechanical Testing Results. Mechanical tests were conducted to obtain the equilibrium modulus in the rubbery region. The kinetic theory of rubber predicts a relationship between equilibrium elastic modulus at temperature well above T_g and the crosslink density.[75-77] The molecular weight between crosslinks (M_c) can be calculated using the equation shown in Scheme 3.15. Originally I planned to use the IMASS Dynostat instrument to measure the equilibrium modulus of these networks, but difficulties in sample preparation made this impractical. Cylindrical samples were required, and these network samples were of a consistency that made it difficult to cut the parallel faces straight or smooth enough to obtain valid measurements. Preliminary work with some sample networks showed that measurements of the equilibrium modulus for a single network composition varied too much from sample to sample to be enable us to make distinctions between the different compositions.

$$G_e = \frac{\rho R T}{M_c}$$

M_c = Av. Molecular Weight Between Crosslinks
R = R=8.314J/°K-Mol,
G_e = Elastic Modulus (Pa)
T = Temperature (413°K)
ρ = Polymer Density

Scheme 3.15. Calculation of the Molecular Weight between Crosslinks using Modulus Measurements.

Table 3.15. GC Analysis of Swelling Effluent: Concentrations Normalized by Initial Sample Weight (Networks A-E, XT).

	Concentration (M/g•L)			
Sample	n-Buthyether	Toluene	Cyclooctene	Chlorobenzene
A	0.000	307.839	1.223	0.000
B	0.000	344.509	1.162	0.254
C	0.029	258.128	1.309	0.283
D	0.000	287.984	1.346	0.345
E	0.000	324.723	1.378	0.363
XT	0.029	253.486	1.457	0.162

Table 3.16. GC Analysis of Swelling Effluent: Network B. (6 Samples)

	Concentration (*M*)			
Sample	n-Buthyether	Toluene	Cyclooctene	Chlorobenzene
B 1	0.009	9.216	0.366	0.096
	0.008	7.446	0.367	0.096
	0.009	8.958	0.368	0.097
B 2	0.007	6.955	0.339	0.092
	0.007	6.700	0.344	0.094
B 3	0.008	8.136	0.348	0.095
	0.007	6.900	0.350	0.095
B 4	0.008	7.537	0.354	0.096
	0.006	6.071	0.354	0.096
B 5	0.000	10.977	0.093	0.022
	0.002	6.543	0.093	0.023
B 6	0.001	8.978	0.068	0.014
	0.001	6.599	0.067	0.014

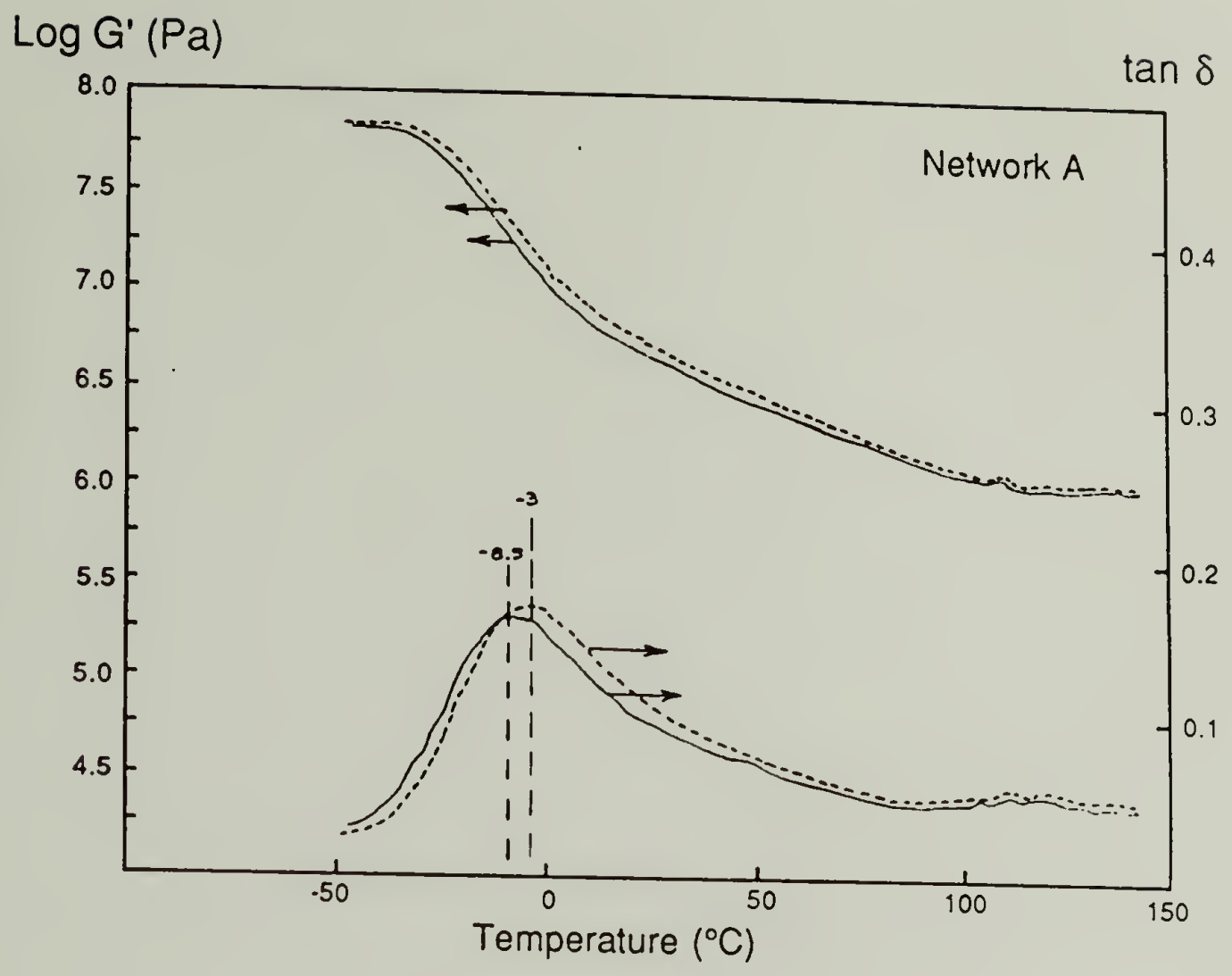
Table 3.17. GC Analysis of Swelling Effluent: Concentrations Normalized by Initial Sample Weight Network B. (6 Samples)

	Concentration (M/g•L)			
Sample	n-Buthyether	Toluene	Cyclooctene	Chlorobenzene
B 1	0.055	54.739	2.177	0.573
	0.049	44.228	2.183	0.573
	0.053	53.207	2.186	0.576
B 2	0.046	45.245	2.205	0.598
	0.046	43.586	2.238	0.612
B 3	0.053	54.071	2.313	0.631
	0.047	45.856	2.326	0.631
B 4	0.050	47.015	2.208	0.599
	0.037	37.870	2.208	0.599
B 5	0.000	248.124	2.102	0.497
	0.045	147.898	2.102	0.520
B 6	0.027	245.838	1.862	0.383
	0.027	180.696	1.835	0.383

These factors were not as critical with the Polymer Labs Dynamic Mechanical Analysis (DMA) instrument, which used thin (1 mm) cylindrical samples to make shear modulus measurements on the samples over a broad temperature range (-50-150°). Scans of Networks A-E and the sample without any TCOD (XT) are shown in Figure 3.12, and the corresponding values of M_c are listed in Table 3.18. The XT sample clearly showed flow-type behavior by the drop in modulus after the rubbery-plateau region, and the samples containing TCOD did not. There was no distinct trend with regard to modulus or M_c to show a change in modulus corresponding to the different concentrations of TCOD in each sample. As the concentration of TCOD decreases, the tan δ peak is generally larger, indicating that the value of G"/G' is larger. We would expect tan δ to increase as the distance between crosslinks increases, because the networks would behave in a more viscous and a less elastic manner. In a second scan of Networks B and XL, the tan δ peak moved to higher temperatures, indicating a chemical change in the sample after the first scan, probably due to crosslinking.

Network Characterization Discussion

Based on the ratio of TCOD to COE/NBE in the monomer mixture, we expected M_c values calculated from swelling and mechanical measurements for the most and the least crosslinked samples to differ by a factor of 17. As seen in Tables 3.11 and Table 3.18 and summarized in Table 3.19, the values of M_c calculated from the swelling data and those based on the DMA measurements indicated that there was very little difference in crosslink density between the samples. Clearly these network samples are more crosslinked than we would expect based on the amount of TCOD in the monomer mixture, i.e. TCOD is not the only source of crosslinking in these systems.



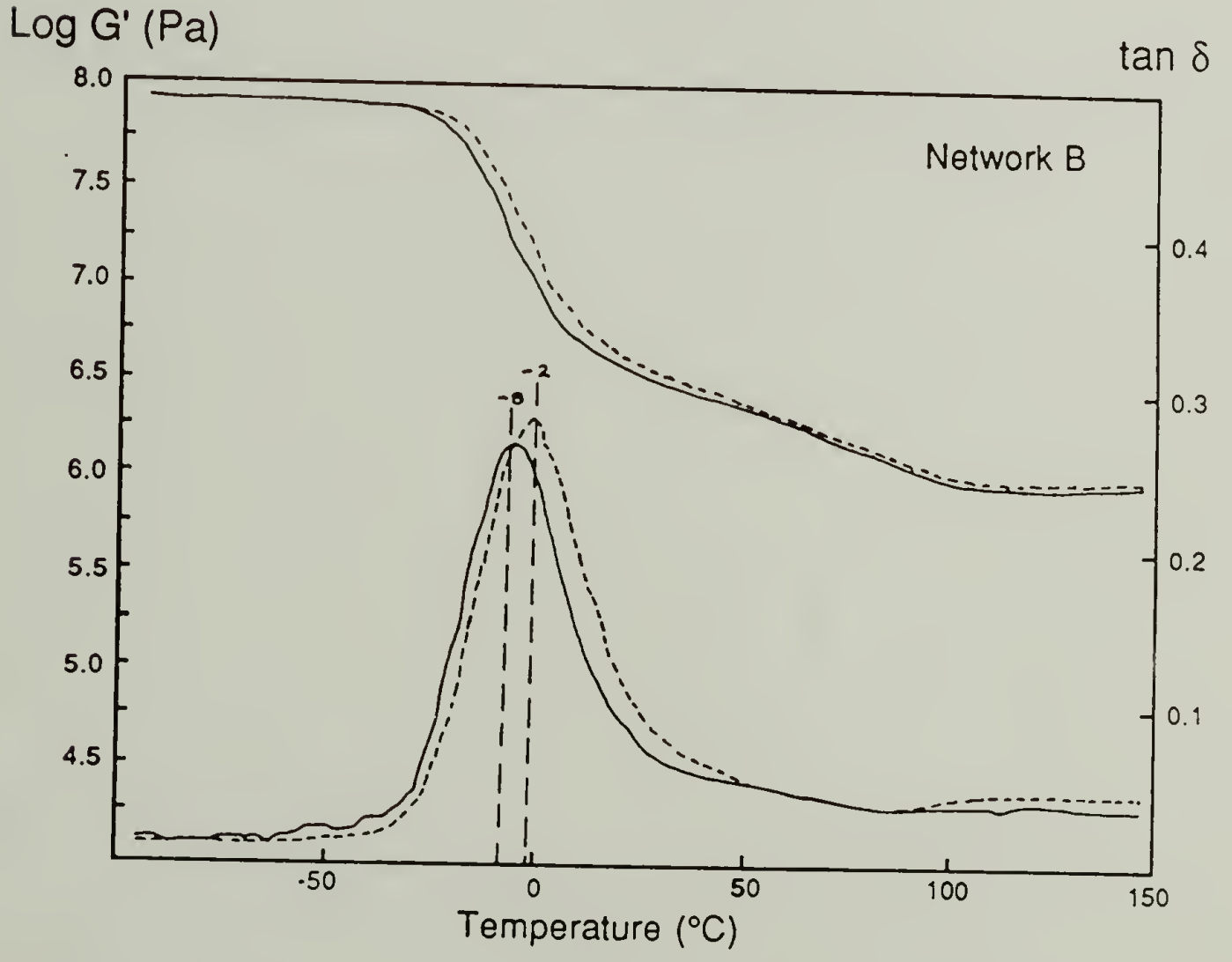
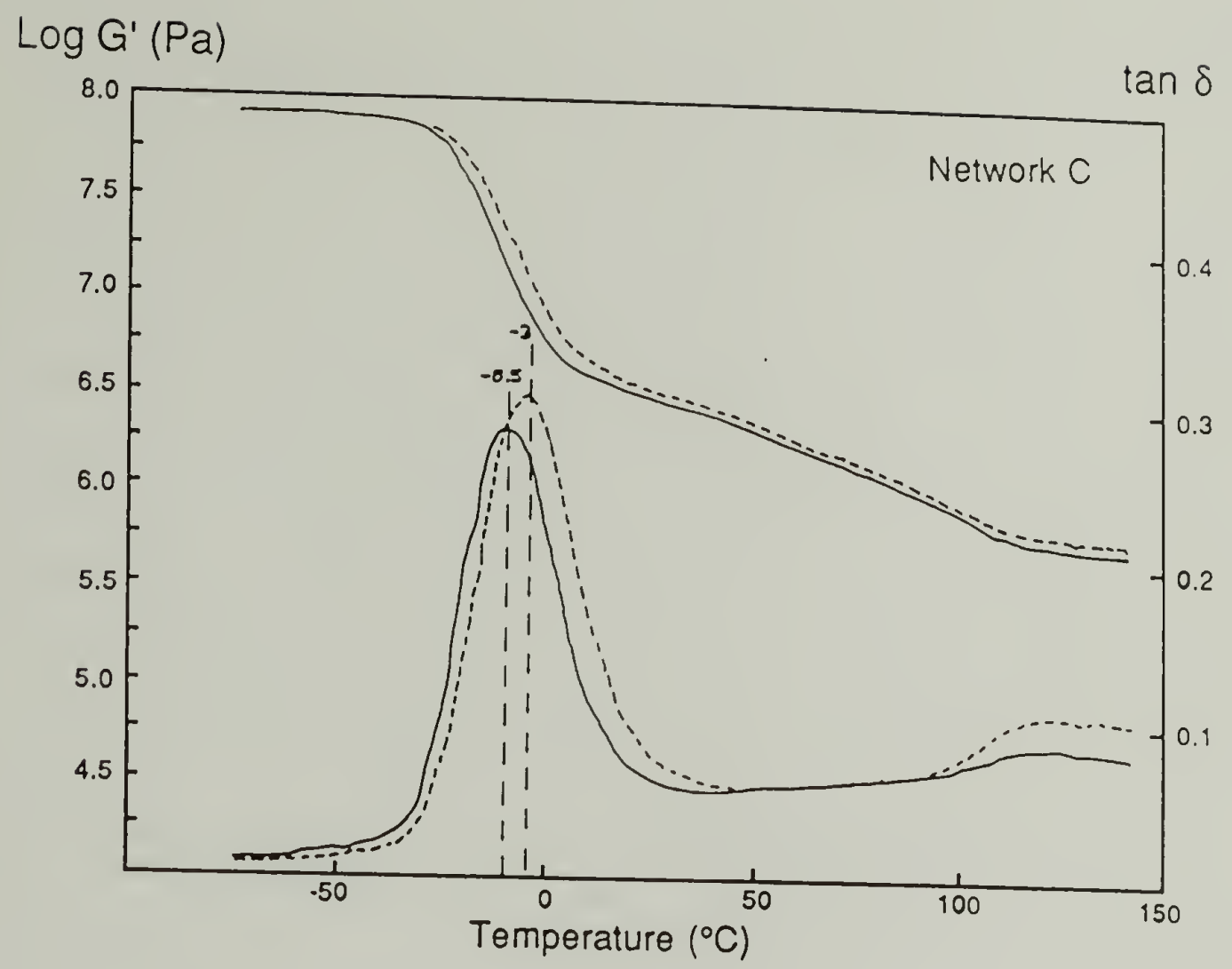


Figure 3.12. DMA Plots of Modulus vs. Temperature for Network Samples A-E, XT.

(Continued Next Page)



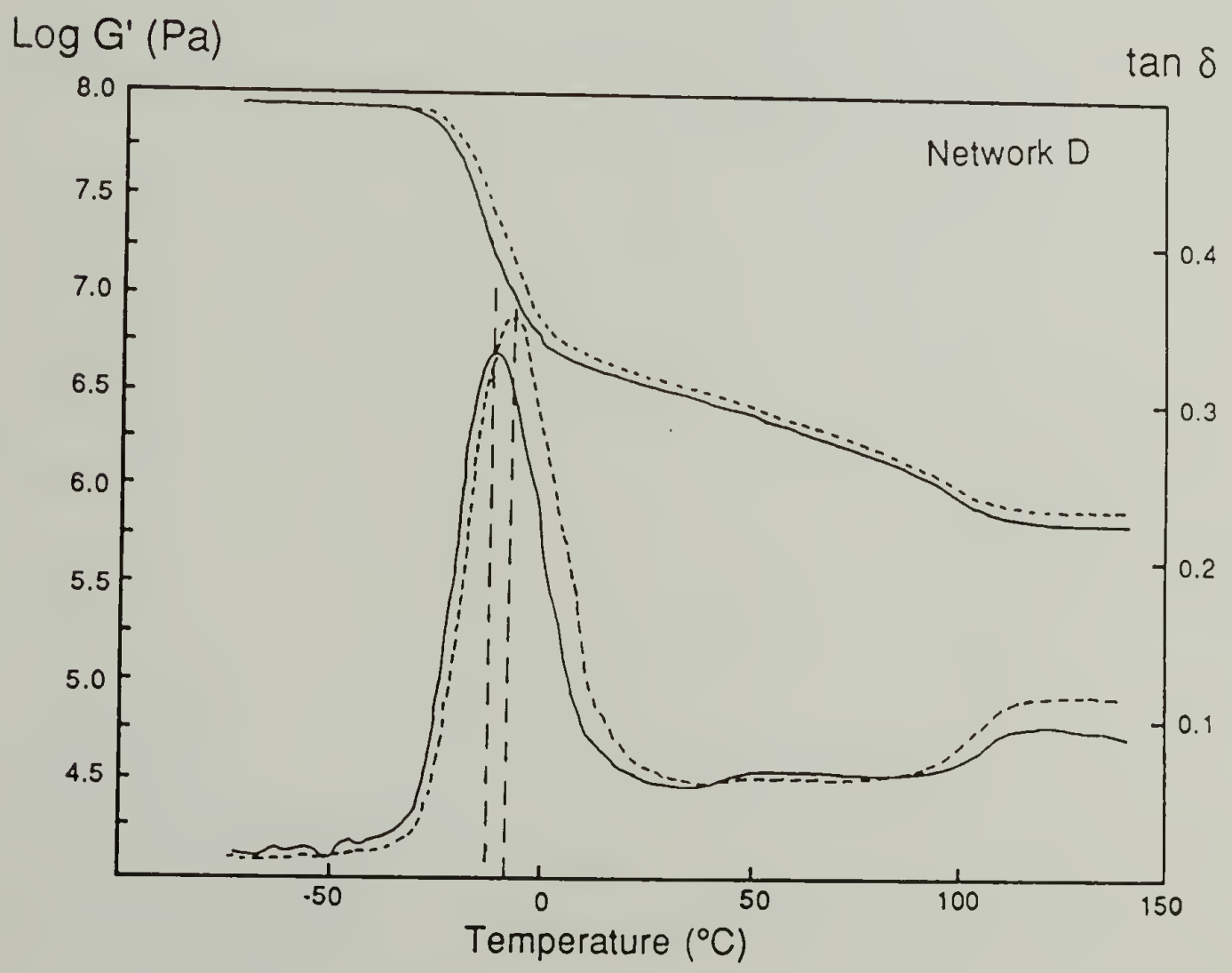
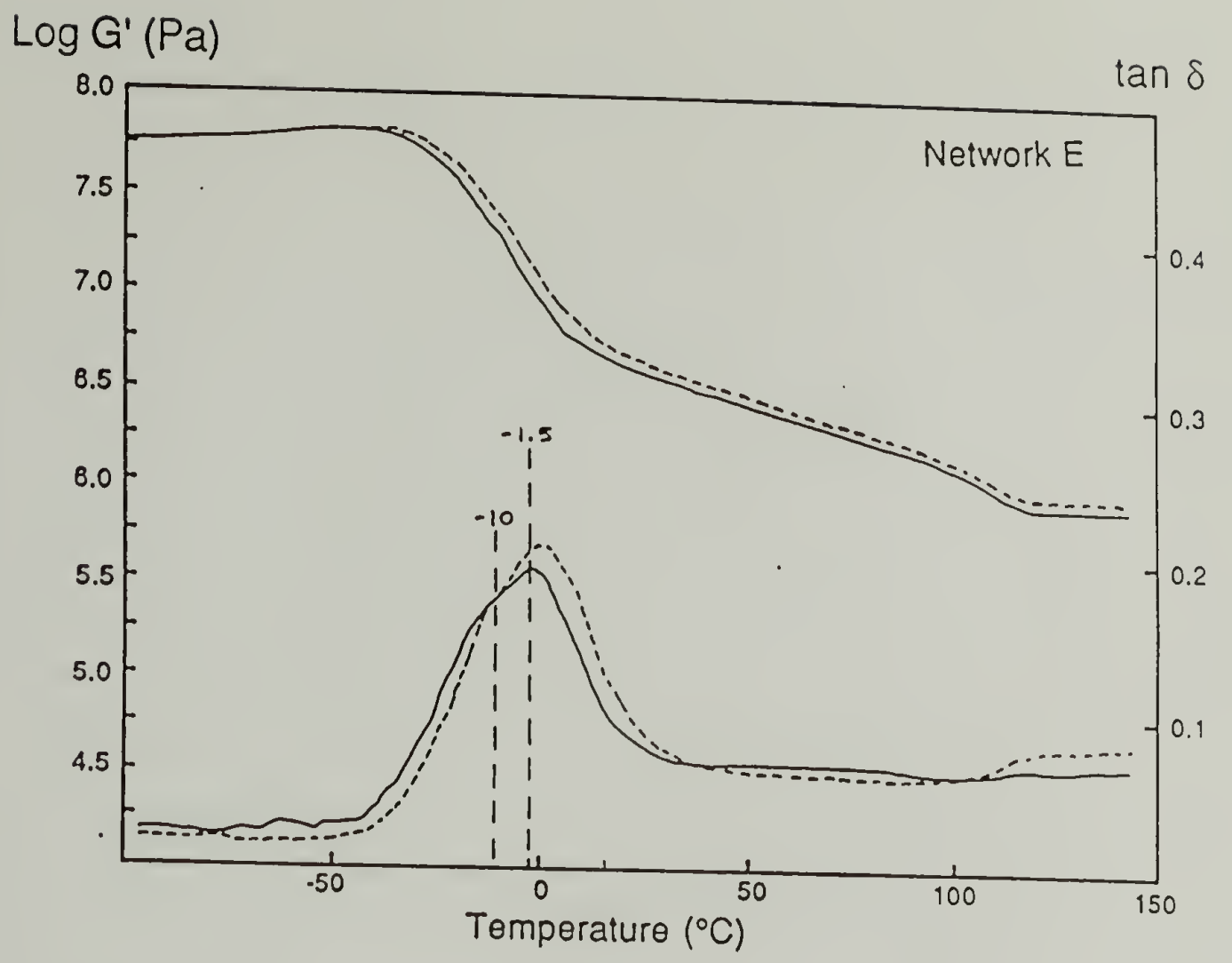


Figure 3.12, Cont.



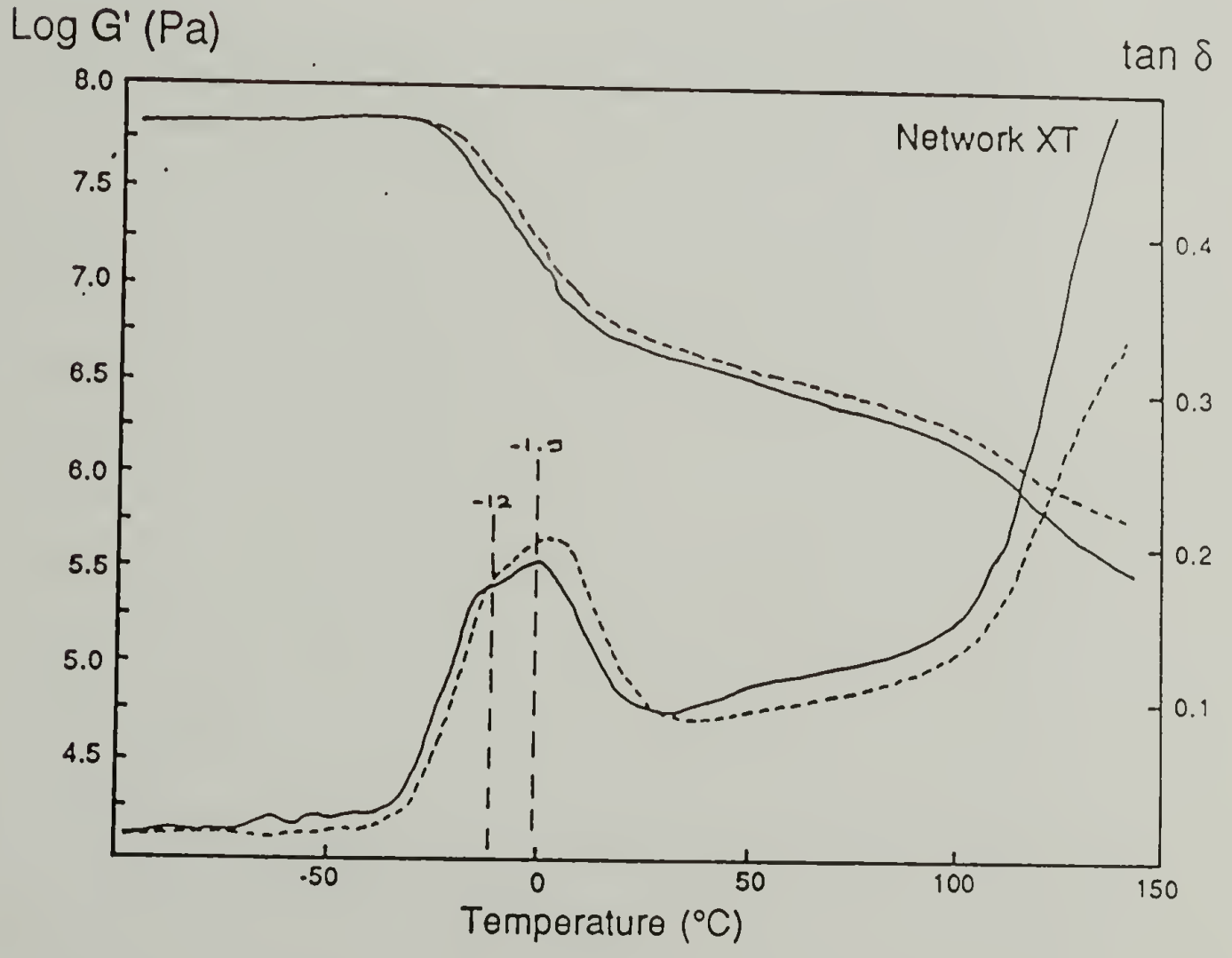
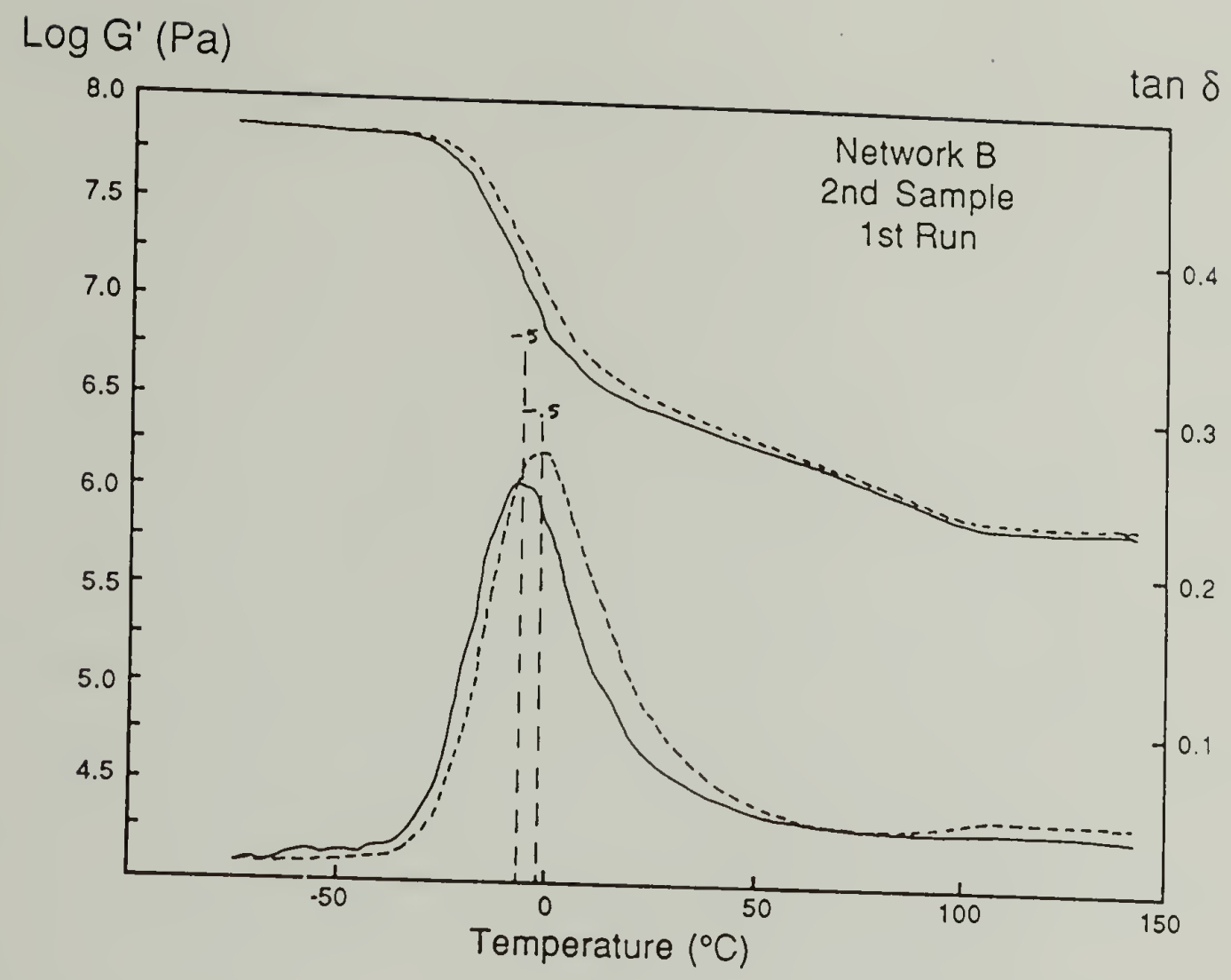


Figure 3.12, Cont.



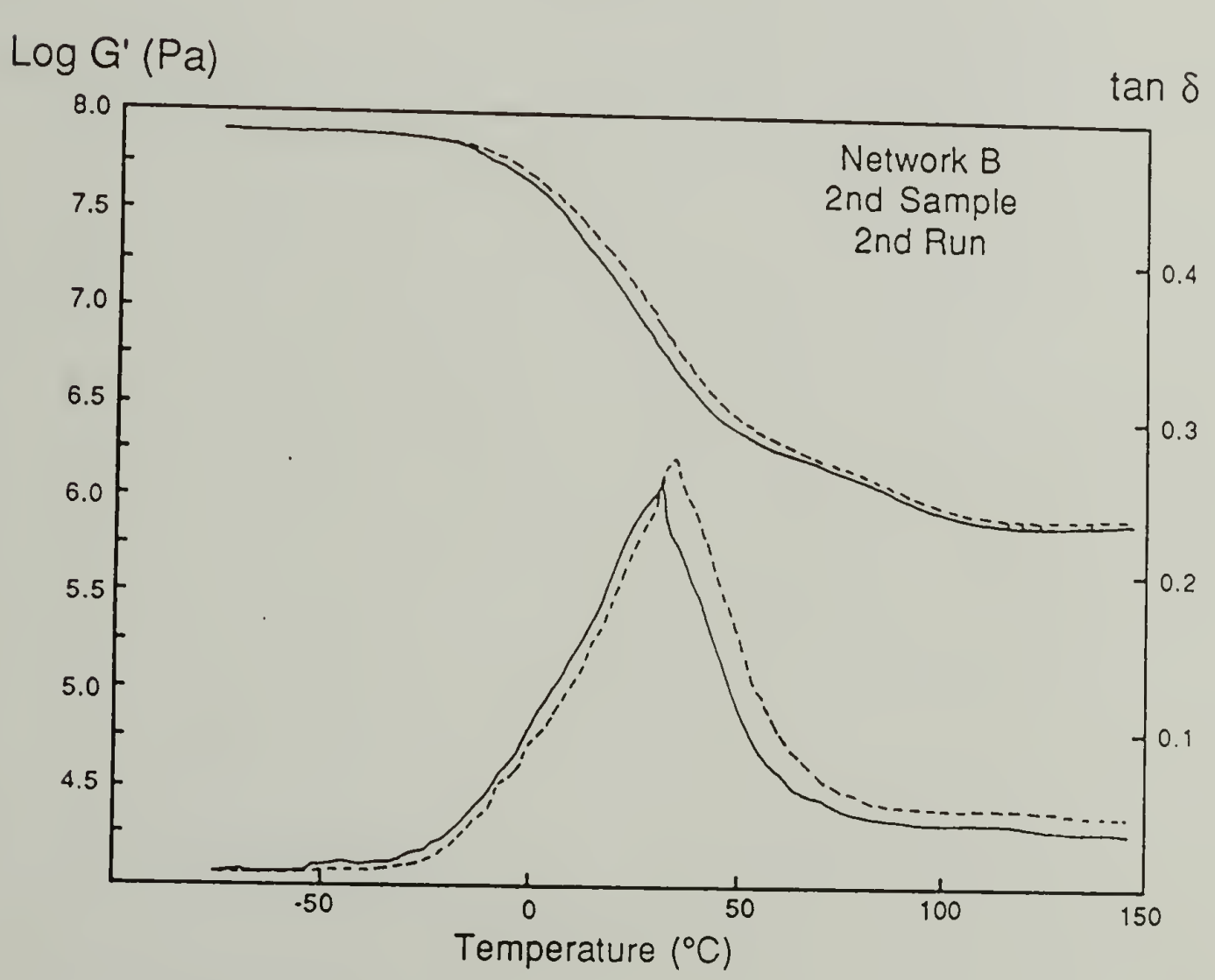
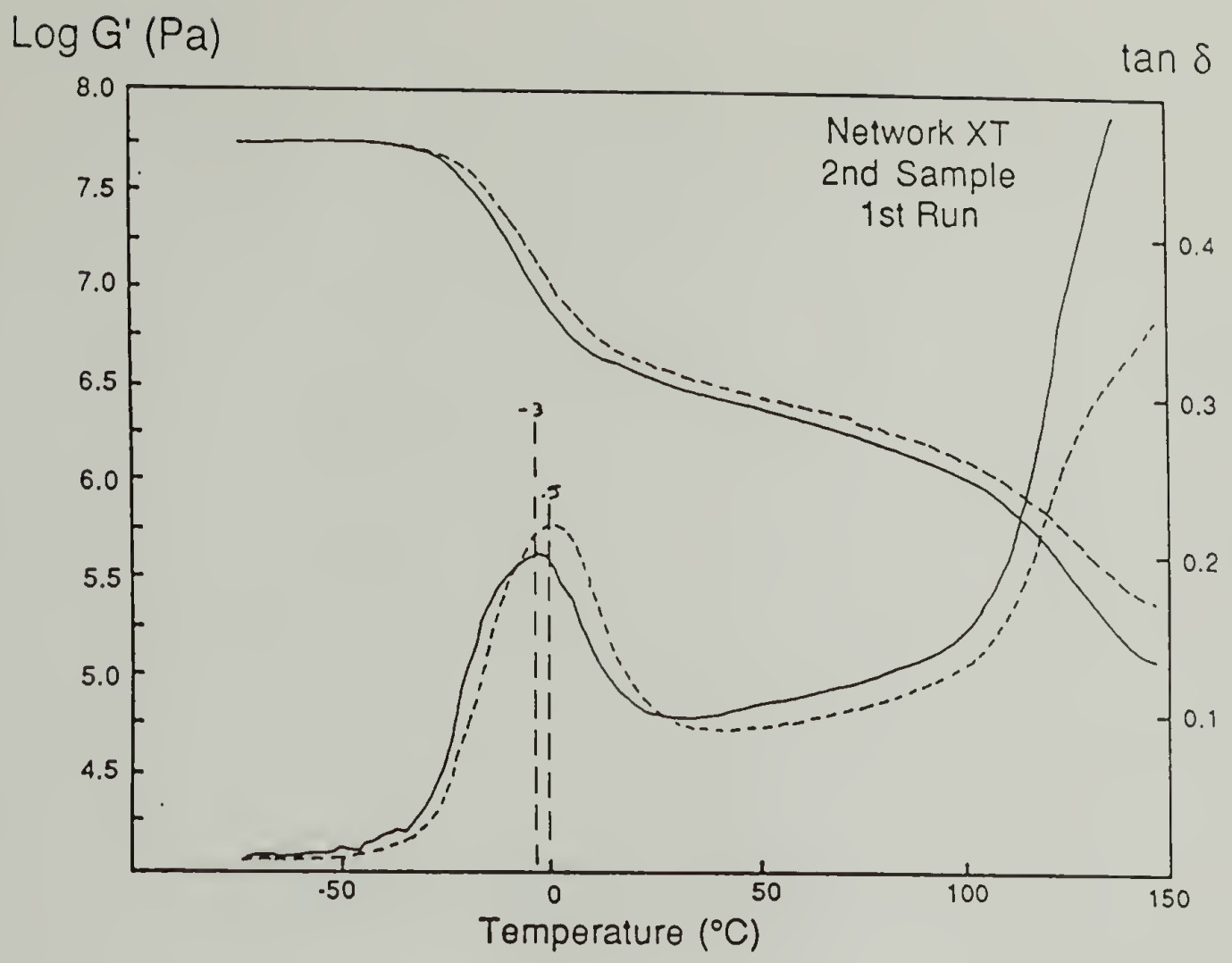


Figure 3.12, Cont.



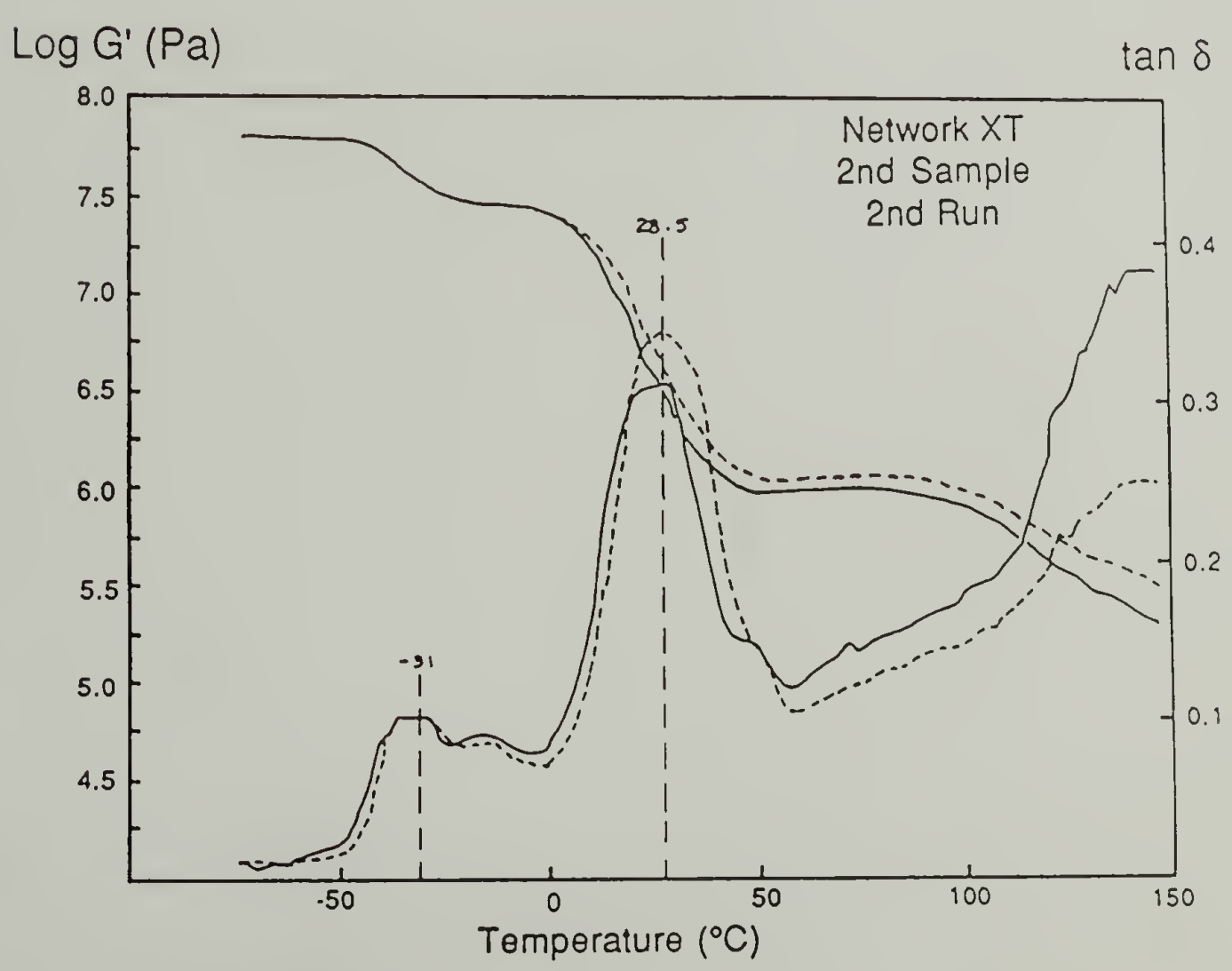


Figure 3.12, Cont.

Table 3.18. M_c Calculated by DMA Modulus Measurements.

Network	Frequency	Log G_e	G_e (Pa)	M_c (g/Mole)
A	10	6.06	11.36E+05	2870
	1	6.03	10.66E+05	3060
B -1	10	5.97	9.38E+05	3477
	1	5.94	8.80E+05	3707
B-2 (1st run)	10	5.92	8.25E+05	3952
	1	5.89	7.74E+05	4213
B-2 (2nd run)	10	5.96	9.09E+05	3590
	1	5.92	8.36E+05	3902
C	10	5.78	5.99E+05	5441
	1	5.72	5.27E+05	6184
D	10	5.87	7.36E+05	4434
	1	5.81	6.39E+05	5104
E	10	5.97	9.26E+05	3522
	1	5.92	8.25E+05	3952
XT-1	10	5.79	6.19E+05	5270
	1	5.54	3.48E+05	9372
XT2 (1st run)	10	5.56	3.59E+05	9077
	1	5.28	1.90E+05	17207
XT2 (2nd run)	10	5.61	4.08E+05	7987
	1	5.42	2.61E+05	12497

At 140C= 413K, R=8.314J/KMol, Ge in Pa

Table 3.19. Comparison of M_c Calculated by Initial Stoichiometry, DMA and Swelling Measurements.

Network	Initial Ratios Mono/TCOD	DMA		Swelling: ∂=.95 X=.45	
		10 Hz	1 Hz	74	93
A	912	2870	3060	805	439
B	1823	3477	3707	632	518
C	4558	5441	6184	815	930
D	8487	4434	5104	648	694
E	15804	3522	3952	1093	1039
XT	—	9077	17207	4573	1920

The presence of residual COE in these samples means that the ratio of monomer to TCOD must be lower than expected in each sample. Because analysis of the swelling effluent did not show TCOD for any of the compositions synthesized, the value of M_c based on the initial stoichiometries must be lower than originally projected. In addition, TCOD units are certainly not the only source of crosslinks in these samples. Oxidative reactions due to the heat of reaction during the polymerization could also have caused crosslinking. More importantly, the backbiting mechanism which occurs because the new double bonds in the polymer chain are also reactive toward metathesis catalysts may be causing a large proportion of rings or loops within the networks. These cyclic oligomers effectively act as crosslinks because they are permanent entanglements. At higher stresses, these entanglements effect the network in the same manner as true crosslinks formed by TCOD. The possibility of producing permanent entanglements of this sort is higher with the Metton system because the polymerizations are carried out with neat monomer and very little solvent. The quick onset of gelation in these samples may keep the polymerization from reaching an equilibrium distribution of oligomers and consequently crosslink densities.

Other entanglements which are not limited by covalent bonds should eventually become untangled during swelling tests, but our swelling tests may not have been run long enough to assume this sort of equilibrium. These entanglements along with the cyclic oligomers are acting as crosslinks, giving the networks higher crosslink density than predicted by the initial stoichiometry. The probability of these types of crosslinks is not affected by the amount of TCOD in each system, except for the fact that samples with more TCOD reached the gel point more quickly and might have an increased tendency to form entangled loops via backbiting.

The values of M_c from the Flory-Huggins calculation show us that the samples are more tightly crosslinked than expected and the M_c values based on modulus show that all of the samples have approximately the same crosslink density, except for the control samples. The presence of extra entanglements obscures the effects of the different concentrations of the crosslinking agent in both types of measurements.

We know from experience that different monomers are incorporated into chains at different rates with metathesis catalysts. Although both COE and NBE were originally present in equimolar quantities, all of the NBE was consumed in these reactions, but small quantities of unreacted COE were extracted from the polymerized samples. If the amounts of NBE and COE incorporated into the samples were not equal, then the idea of using an average of the two molecular weights in the calculations was not correct. In addition, if TCOD was incorporated faster than COE or NBE, then the crosslinks may not be evenly distributed along the chains. Although it may not be completely appropriate to apply these calculations to non-ideal networks, the swelling and mechanical tests show that the differences in crosslink density cannot be explained by the changes in the concentration of TCOD between samples.

A less complex method for making samples using a single monomer besides the crosslinking agent would be preferable because it would eliminate ambiguities concerning the molecular weight of a single unit and the relative rates of monomer incorporation into the networks. The Metton™ catalyst may not be optimal for our purposes. A simpler catalyst system which did not require the addition of solubilizers or stabilizers would improve our ability to make consistent samples from a given batch of monomer. The increased number of entanglements, inherent in a polymerization with neat monomer, add to the degree of imperfection of the networks.

Characterization of crosslinked networks is not limited to the swelling and mechanical measurements described here. Other techniques include measurement of the modulus of swollen samples, creep and mechanical damping measurements for rubbers, and shifts in the glass transition temperature. We also have an additional characterization method at our disposal which is not hindered by the presence of these covalent entanglements because we can take advantage of metathesis catalysts. Several groups have examined the microstructure and degree of network perfection of polybutadiene networks using metathesis "degradation" reactions.[55-56,80-82] This technique takes advantage of the ability of metathesis catalysts to act as chain scissors. The $WCl_6/SnMe_4$ system is especially common to these types of studies involving internal olefins. Conditions such as temperature, concentration and reaction time can be adjusted to stop the degradation at different distributions of oligomers, monomer and polymer. Characterization of the type and distribution of the fragments would give us an indication of the type of building blocks present in the original network structure.

Conclusions

We have synthesized a crosslinking agent for metathesis polymerizations which can be used to create crosslinked networks. Solution studies with the $WCl_6/SnMe_4$

catalyst system showed that TCOD could be homopolymerized and also copolymerized with COE. The latter studies showed that the addition of TCOD to a polymerization in progress resulted in a dramatic increase in the viscosity and in the molecular weight, based on visual and GPC results.

A series of crosslinked network samples was synthesized in solid form for physical characterization studies. Testing these networks to determine the the relationship between the concentration of TCOD and crosslink density was more complicated than we anticipated, because TCOD was not the only source of crosslinks in our system The values for M_c obtained from both swelling and dynamic mechanical measurements to determine modulus showed that the crosslink densities of the samples were much different than those predicted by the amount of TCOD present, due to the presence of other types of crosslinks, i.e. entanglements which were artifacts of the polymerization process with neat monomer. However the dramatic increase in the degree of swelling and the drop in modulus after the rubbery plateau region for the control samples were clear indications that the samples containing the crosslinking agent were distinctly different than those which did not.

The original goal of developing a crosslinking agent for metathesis was to be able to tailor the number and placement of crosslinks in a networks. Now that we have established that TCOD can function as a crosslinking agent, different catalyst systems could be used to develop the potential of TCOD as a metathesis crosslinking agent. The well characterized alkylidene catalysts developed by Grubbs and Schrock open up new dimensions in network construction.[44-48,83] For example, Schrock has recently published a paper showing the synthesis of star polymers using the norbornadiene dimer as the hub. The key to using these catalysts is selecting monomers with suitable differences in reactivity; TCOD represents a different crosslinking agent than one derived from the norbornadiene dimer because of the difference in structure between the

propagating carbenes. As a result, TCOD would be useful for crosslinking systems based on monomers other than norbornene derivatives. If we could control network perfection through the use of these types of catalysts, then ultimately crosslinking agents such as TCOD could be used to create networks and membranes with pore sizes which were predetermined on the molecular level. The addition of TCOD to the set of metathesis tools is a significant contribution to our ability to influence macromolecular architecture.

References

1. March, J. Advanced Organic Chemistry, Wiley-Interscience, New York, 1985, 3rd ed. p. 914, 924.

2. Feast, J.; Harper, K. *J. Mol. Catal.* **1985**, *28*, 293.

3. Reyx, D.; Croissandeau, M. *Makromol. Chem.* **1982**, *183*, 1371.

4. Reyx, D.; Hamza, M.; Campistron, I. *J. Mol. Catal.* **1987**, *42*, 289.

5. Van Dam, P. B.; Mittelmeijer, M.C.; Boelhouwer, C. *Chem. Commun.* **1972**, 1221.

6 Mol, J. C. *J. Mol. Catal.* **1982**, *15*, 35.

7. Levisalles, J.; Villeman, D. *Tetrahedron* **1980**, *36*, 3181.

8 Castner, K. F.; Calderon, N. *J. Mol. Catal.* **1982**, *15*, 47.

9. Brunthaler, J. K.; Stelzer, F.; Leising, G. *J. Mol. Catal.* **1985**, *28*, 393.

10. Hocks, L.; Noels, A.; Hubert, A.; Teyssie, P. J. Org. Chem. **1976**, *41*, 1631.

11. Uchida, A.; Ishikawa, T.; Takagi, M. *Rec. Trav. Chim. Pays-Bas* **1977**, *96*, M13.

12. Wengrovius, J. H.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Amer. Chem. Soc.* **1982**, *104*, 1739.

13. Ivin, K. J. Olefin Metathesis, Academic Press, London, 1983. p. 121.

14. Mol, J. C. *Chemtech*, **1983**, *13*, 250.

15. Kapteijn, F.; Van Der Steen, A. J.; Mol, J. C. *J. Chem. Therm.* **1983**, *15*, 147.

16. Mol, J. C.; Moulijn J. A. *Adv Catal.* **1975**, *24*, 131.

17. Otton, J.; Colleuille, Y.; Varagnat, J. *J. Mol. Catal.* **1980**, *8*, 313.

18. Ellison, A.; Coverdale, A. K.; Dearing, P. F. *J. Mol. Catal.* **1985**, *28*, 141.

19. Mol, J. C. *J. Mol. Catal.* **1985**, *28*, 133.

20. Ivin, K. J.; Lapienis, G.; Rooney, J. J. *Makromol. Chem.* **1982**, *183*, 9.

21. Patton, P.A.; McCarthy, T. J. *Macromolecules* **1987**, *20*, 778.

22. Verkuijlen, E.; Kapteijn, F.; Mol, J. C.; Boelhouwer, C. *Chem. Commun.* **1977**, 198.

23. Ast, W.; Rheinwald, G.; Kerber, R. *Rec. Trav. Chim. Pays-Bas* **1977**, *96*, M127.

24. El Saafin, I. F.; Feast, J. W. *J. Mol. Catal.* **1982**, *15*, 61.

25. Thoi, H. H.; Reddy, B. S. R.; Rooney, J. J. *J. Chem Soc., Faraday Trans. I* **1982**, *78*, 3307.

26 Stelzer, F.; Brunthaler, J. K.; Leising, G.; Hummel, K. *J. Mol. Catal.* **1986**, *36*, 135.

27. Alimuniar, A. B.; Edwards, J. H.; Feast, W. J. *J. Mol. Catal.* **1985**, *28*, 313.

28. Patton, P. A. *Ph. D. Dissertation* University of Massachusetts, Amherst, 1988.

29. Norton, R. L. *Ph. D. Dissertation* University of Massachusetts, Amherst, 1989.

30. Hocker, H.; Reiman, L.; Reibel, K. *J. Mol. Catal.* **1980**, *8*, 191.

31 Masuda, T.; Hasegawa, K.; Higashimura, T. *Macromolecules* **1974**, *7*, 728.

32. Laverty, D. T.; McKarvey, M. A.; Rooney, J. J.; Stewart, A. *Chem. Commun.* **1976**, 194.

33. Grubbs, R.H., in Compendium of Organometallic Chemistry, Wilkenson,G., Stone, F. G. A.; Asbel, E. W. Eds.; Pergamon Press, Ltd.; Oxford, 1982. Vol. 8, p. 499.

34. Reyx, D.; Campistron, I.; Hamza, M. *J. Mol. Catal.* **1986**, *36*, 101.

35. Reyx, D.; Campistron, I.; Heiling, P. *Makromol. Chem.* **1982**, *183*, 173.

36. Ast, W.; Rheinwald, G.; Kerber, R. *Makromol. Chem.* **1976**, *177*, 1349.

37 . Reyx, D. *J. Mol. Catal.* **1980**, *8*, 325.

38. Ast, W.; Rheinwald, G.; Kerber, R. *Rec. Trav. Chim. Pays-Bas* **1977**, *96*, M127.

39. Wiberg, K. B.; Williams, V.Z.; Fredrich, L.E. *J. Am. Chem. Soc.* **1970**, *92*, 564.

40. Cope, A.C.; Tiffany, B. D. *J. Am. Chem. Soc.* **1951**, *73*, 4158.

41. Cope, A.C.; Schaeren, S. F.; Trumbull, E. R. *J. Am. Chem. Soc.* **1954**, *76*, 1096.

42. Verkuijlen, E.; Dirks, R. J.; Boelhouer, C. *Rec. Trav. Chim. Pays-Bas* **1977**, *96*, M86.

43. Balcar, H.; Dosedlova, A.; Matyska, B. *J. Mol. Catal.* **1987**, *41*, 367.

44. Gilliom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 733.

45. Risse, W.; Wheeler, D. R.; Cannizzo, L.; Grubbs, R. H. *Macromolecules* **1989**, *22*, 3205.

46. Wallace, K. C.; Schrock, R. R. *Macromolecules* **1987**, *20*, 450.

47. Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; Dimare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875.

48. Schrock, R. R.; DePue, R. T.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423.

49. Ivin, K. J.; Saegusa, T. Ring-Opening Polymerization, Elsevier, London **1984**. Vol. I.

50. Odian, G. Principles of Polymerization, Wiley-Interscience, New York, **1985**. 2nd Ed, p. 268.

51. Patton, P.A.; Lillya, C. P.; McCarthy, T. J. *Macromolecules* **1986**, *19*, 1266.

52. Holtrup, W.; Streck, R.; Zaar, W.; Zerpner, D. *J. Mol. Catal.* **1986**, *36*, 127.

53. Hocks, L.; Berck, D.; Hubert, A. J.; Teyssie, P. *J. Polym. Sci., Polym. Lett.* **1975**, *13*, 391.

54. Kumar, V. G., Hummel, K. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 1183.

55. Ivin, K. J. Olefin Metathesis, Academic Press, London, 1983. Chapter 16.

56. Hummel, K.; Lechner, H.; Pongratz, T. *J. Mol. Catal.* **1986**, *36*, 177.

57. Hocks, L.; Berck, D.; Hubert, A. J.; Teyssie, P. *J. Polym. Sci., Polym. Lett. Ed.* **1975**, *13*, 391.

58. Hocks, L.; Noels, A.; Hubert, A.; Teyssie, P. *J. Org. Chem.* **1976**, *41*, 1631.

59. Korshak, Y. V.; Dolgoplosk, B. A.; Tlenkopachev, M. A. *Rec. Trav. Chim. Pays-Bas* **1977**, *96*, M64.

60. Tlenkopachev, M. A.; Kop'eva, I. A.; Bychkova, N. A.; Korshak, Y.V.; Timofeeva, G. I.; Tinyakova, B. A. *Dokl. Chem. (Engl.)* **1976**, *227*, 279

61. Schrock, R. R.; Krouse, S. A.; Knoll, K.; Feldman, J.; Murdzek, J. S.; Yang, D. C. *J. Mol. Catal.* **1988**, *46*, 243.

62. Canjii, E.; Perner, H. *Rec. Trav. Chim. Pays-Bas* **1977**, *96*, M70.

63. Canjii, E.; Perner, H. *Makromol. Chem* **1978**, *179*, 567.

64. Thorn-Csanyi, E.; Perner, H. *J. Mol. Catal.* **1986**, *36*, 187.

65. Dolgoplosk, B. A.; Kopieva, I. A.; Oreshkin, I. A.; Tiniakova, E. I. *Eur. Polym. J.* **1980**, *16*, 547.

66. Holtrup, W.; Streck, R.; Zaar, W.; Zerpner, D. *J. Mol. Catal.* **1986**, *36*, 153.

67. Hamilton, J. G.; Ivin, K. J.; Rooney, J. J. *J. Mol. Catal.* **1986**, *36*, 115.

68. Klavetter, F. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 7807.

69. Paquette L. A.; Carmody M. J. *J. Amer. Chem Soc.* **1976**, *98*, 8175.

70. Avram, M.; Marica, E.; Dinulescu, I.; Farcasiu, M.; Elian, M.; Mateescu, G.; Nenitzescu C. D. *Chem. Ber.* **1964**, *97*, 383.

71. Breslow, D. S. *Chemtech* **1990**, September.

72. Klosiewicz, D. W. **U.S. Patent** 4,400,340 (1983).

73. Matejka, L.; Houtman, C.; Macosko, C. W. *J. Appl Polym. Sci.* **1985**, *30*, 2787.

74. Dall'Asta, G.; Manetti, R. *Eur. Polym. J.* **1968**, *4*, 145.

75. Flory,P. J. Principles of Polymer Chemistry, Cornell Univ. Press, Ithaca, 1953.

76. Quislel, J. P.; Mark, J. E. *J. Chem Ed.* **1987**, *64*, 491.

77. Treloar, L. R. G. The Physics of Rubber Elasticity. Oxford, London, 1958.

78. Zang, Y. H.; Muller, R.; Froelich, D. *Polymer* **1989**, *30*, 2060.

79. Brandrup, J; Immergut, E.H. Polymer Handbook. Wiley Interscience, New York, 1975.

80. Hummel, K. *J. Mol. Catal.* **1985**, *28*, 381.

81. Stelzer, F.; Hobisch, G.; Pongratz, T.; Hummel, K. *J. Mol. Catal.* **1988**, *46*, 433.

82. Thorn-Csanyi, E.; Perner, H. *J. Mol. Catal.* **1986**, *36*, 187.

83. Schrock, R. R. *Macromolecules* **1987**, *20*, 450.

PART II. APPLICATION OF CARBON-HYDROGEN BOND ACTIVATION TO THE SURFACE OXIDATION OF POLYPROPYLENE AND POLYETHYLENE

CHAPTER 4

INTRODUCTION

Overview

The goal of this project was to study the oxidation of polypropylene and polyethylene surfaces, using reagents that have traditionally been applied toward the C-H bond activation of small molecules. We wanted to manipulate reaction conditions such that the oxidation products were limited to alcohols and that the modifications took place in a surface-selective manner.

Ideally, a surface-selective reaction modifies the chemical architecture of the surface and create a two dimensional array of functional groups, without destroying the physical integrity of the virgin polymer. In our research group, we have developed several unique surface modification reactions by applying simple, common sense organic chemistry ideas to reactions at polymer surfaces.[1-9] Initially, we concentrated on chemically resistant polymers to develop an understanding of how to control surface modifications with respect to the number and type of functional groups, their location within the modification depth and the sharpness of the interface between modified and unmodified polymer. In the course of this effort, we developed a variety of ways to attach functional groups to polymer surfaces. We would now like to expand our expertise to more reactive polymers, while at the same time maintaining the same standards of elegance, with regard to the surface-selectivity and specificity of the chemical transformation.

The objective of this work was to develop a generic polymer surface modification which would place a single type of functional group on a polymer in a surface selective

manner, without causing large changes in surface topography. As a logical starting point for this investigation, I proposed the activation of the C-H bonds on the surface of saturated hydrocarbon polymers to create hydroxylated surfaces, as shown in Scheme 4.1. Selective oxidation of the C-H bonds on these polymer surfaces to alcohol groups would transform a low surface energy polymer into a wettable solid. The bulk properties of the material would remain the same, but the hydroxyl groups would provide reactive handles for further functionalization and would enhance adhesive properties.

Scheme 4.1. Hydroxylation of Hydrocarbon Polymers.

C-H bond activation chemistry was chosen as the focus of this work because it can be applied to a variety of polymer systems, and because these types of reactions have been investigated and reported extensively in the literature.[10-13] Both aliphatic and unsaturated substrates have been successfully activated, but selective functionalization, i.e. the formation of one major product, continues to be a synthetic challenge. Alkanes are more difficult to activate than alkenes or aromatics because of their increased ionization potentials and their lack of bond polarizability. In many cases, brute force conditions such as high temperatures or strong acids have been employed for the oxidation of saturated hydrocarbons.[14-17] These methods lead to a broad distribution of products, ranging from alcohols to carboxylic acids, and are not appropriate for selective functionalization. Milder

conditions and more specific functionalization are possible with the use of transition metal catalysts[10-11,18-19] as well as some non-metallic reagents such as super-,[20] percarboxylic-[21-22] and perbenzoic acids.[23-24] These less severe methods have the additional advantage that the reactions can take place at lower temperatures and in solvents which do not swell most polyolefins. Surface selectivity and the sharpness of the interface between the modified and unreacted layers can be controlled by choosing combinations of reaction solvent and temperature which prevent the polymers from swelling, and by avoiding reagents that would corrode or pit the surface.[1-3]

The difficulty in applying most of the reagents capable of aliphatic C-H bond activation toward polymer surfaces is that the products of these oxidations are more reactive than the original substrates and several different oxidation products are obtained.[10-13] In the case of small molecules, the product mixtures can be separated using standard purification techniques such as distillation or chromatography, but these options are not available for polymer surface modification. Alternatively, in solution, the initial products (alcohols) can sometimes be isolated by stopping the reaction before high degrees of conversion have been obtained,[23] but this limits the number of groups that can be placed on the surface.

Reagents

The reactions proposed here were chosen because they are reported to produce high yields of alcohols from alkanes, without further oxidation to ketones or carboxylic acids. We also chose soluble systems, because insoluble reagents further complicate what is by necessity a heterogeneous reaction.

Stannous Chloride/Oxygen

The stannous chloride/O_2 oxidation of cyclohexane developed by Shilov[10,25-27] was particularly attractive for our purposes because an excess of Sn^{2+} insures that the cyclohexanol formed does not become further oxidized to cyclohexanone. Hydrocarbon autoxidation with Sn^{2+} in water/organic media proceeds via a branched chain mechanism in which the alkanes present in solution are attacked by hydroxyl radicals. The qualitative equation for the formation of alcohols in this system and the mechanism for the oxidation of cyclohexane in this system are shown in Scheme 4.2 for R= cyclohexane.

Qualitatively: $RH \xrightarrow{HO^{\bullet}} R^{\bullet} \xrightarrow{O_2} RO_2^{\bullet} \longrightarrow ROH$ $\qquad R = C_6H_{12}$

(1) $RH + HO^{\bullet} \longrightarrow H_2O + R^{\bullet}$

(2) $R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet}$

(3) $RO_2^{\bullet} + Sn(II) \xrightarrow{H_2O} \begin{cases} \longrightarrow RO_2H + Sn(III) \\ \longrightarrow RO^{\bullet} + Sn(IV) \end{cases}$

(4) $RO_2H + Sn(II) \longrightarrow \begin{cases} \longrightarrow RO^{\bullet} + Sn(III) \\ \longrightarrow ROH + Sn(IV) \end{cases}$

(5) $RO_2H + Sn(III) \longrightarrow RO^{\bullet} + Sn(IV)$

(6) $RO^{\bullet} + RH \longrightarrow ROH + R^{\bullet}$

(7) $RO^{\bullet} + Sn(II) \xrightarrow{H_2O} ROH + Sn(III)$

Scheme 4.2. Stannous Chloride/Oxygen Oxidation of Hydrocarbons: R= Cyclohexane.

Shilov found that cyclohexanol was the major product when an excess of Sn^{2+} was present, although small quantities of cyclohexanone were formed under some conditions. Other studies[28,29] have shown that the presence of additional reducing agents such as elemental tin or hydrazobenzene can lead to improved yields of the alcohol, because they help maintain a high concentration of Sn^{2+}. Cuprous and ferrous chlorides also hydroxylate aliphatic substrates in a manner similar to the $SnCl_2$ system.[28]

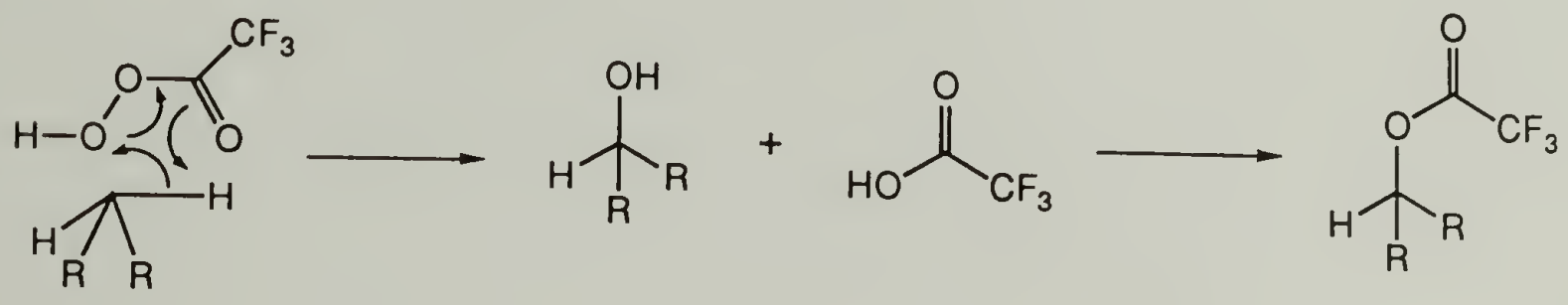
Shilov reported that the yield of cyclohexanol reaches a maximum when the concentration of water in acetonitrile (reaction solvent mixture) reaches 10 M. As the water concentration was further increased, Shilov reported that the yield of product alcohols was directly related to the solubility of cyclohexane in water.[25] Because reactions at polymer surfaces are already heterogeneous, this solubility effect is not a factor and the alcohol yield may be even higher in pure water solutions. Typically, the stannous and cuprous chloride oxidations are carried out in water, acetonitrile or acetone. These are not good solvents for saturated hydrocarbon polymers,[30] and sharp interfaces between modified and unreacted polymer should be possible.

Benzoyl Peroxide/ Methanol

Tsubokawa reported that alcohols were grafted onto the surface of carbon black by reaction with benzoyl peroxide, using the appropriate alcohol as solvent.[31] Although carbon black may contain many more active (aromatic) C-H bonds than those available at an aliphatic polymer surface, this system should be sufficiently active to place alcohol groups on hydrocarbon polymer surfaces. If methanol is the solvent, a primary alcohol surface should be obtained. This should provide us a reactive handle of optimal reactivity for further functionalization on the surface, i.e. reaction with electrophiles.

Trifluoroperacetic Acid

The third reagent identified in our survey of the C-H bond activation literature was trifluoroperacetic acid (TFPAA) which when used for the oxidation of alkanes, produces an equilibrium mixture of secondary alcohols and the corresponding trifluoroacetate esters.[21,32-33] Reaction with substrates containing tertiary carbons produces ketones plus some rearrangement products. The basic mechanism for alkane hydroxylation is shown below in Scheme 4.3.



Scheme 4.3 Mechanism for Alkane Hydroxylation with Trifluoroperacetic Acid.

When Deno reacted cyclohexane in the presence of 15-100% excesses of TFPAA, cyclohexanol was not further oxidized to cyclohexanone nor were there further oxidation products of cyclohexanone i.e. ε-caprolactone.[21] For linear chains, the hydroxyl groups are introduced on chain positions remote from electronegative substituents. For example, the reaction of 1-decanol with TFPAA yields predominantly 1,10-decanediols. Yields and conversions were limited in the solution case by subsequent elimination, epoxidation and conversion to vicinyl glycols.

At first, the binary mixture of functional groups produced in this reaction does not seem optimal to accomplish our original goal of preparing a two dimensional surface with a single array of functional group handles. However, the trifluoroacetate groups should be easily cleaved via base hydrolysis to give a surface of predominantly hydroxyl groups.

In this case, reaction at a surface may work in our favor. In the case of the solution reaction, the initial alcohol products are readily converted to trifluoroacetates. When the product alcohols are constrained to a surface, the conversion may not be as rapid or as complete, and the mixture of functional groups may not be as great a problem.

meta-Chloroperbenzoic Acid

As a fourth alternative, *m*-chloroperbenzoic acid (MCPBA) is a known hydroxylation agent for bridgehead carbons.[24] The secondary carbon atoms in these systems do not react with MCPBA, implying that only the tertiary carbon atoms of the hydrocarbon substrates will participate in the reaction. We hoped that the tertiary sites on polypropylene would be similar enough to the strained bridgehead carbons that we would achieve selective oxidation at the tertiary sites.

Several other substituted perbenzoic[23] and peracetic[22] acids are known to activate C-H bonds, but considerable yields of ketones result from the oxidation of secondary alcohols in these systems. We surveyed the four reactions described above and then choose the most promising one for an in-depth investigation into the nature of the products under various conditions.

Substrates

Many of the reagents that are effective oxidizing agents for alkanes show a marked selectivity for tertiary carbon atoms because they take place via radical or carbocation intermediates.[10-13] In the hydroxylation of isopentane with the $SnCl_2$ system in acetonitrile, Shilov[10] found that reaction at tertiary carbons was preferred to attack at secondary or primary sites by a ratio of 12.5/5.1/1. It was difficult to determine *a priori* which of the saturated hydrocarbon polymers would be better as initial substrates for the

investigation of C-H bond activation at polymer surfaces. Polypropylene should be more reactive toward these oxidizing reagents than polyethylene because of its tertiary carbon atoms, but the heterogeneous nature of these reactions may enhance the effects of steric hindrance from the methyl groups at the surface, thus rendering polyethylene a better candidate. Exploratory reactions were carried out with both substrates to determine which was preferable.

Oxidation of polypropylene and polyethylene has been studied by other groups using a variety of reagents, including strong acids,[14-1724] plasma treatments[34,35] and ozone.[36] The corrosive nature of some of these reactions resulted in rough surfaces and significant losses of substrate material. As a rule, the modifications could not be limited to a single functional group and a range of oxidized species were present in the final products. We hoped that the C-H bond activation reactions that are described above would be both more surface selective and more specific with respect to their distribution of products. The oxidation reactions described above should result in a surface selective hydroxylation, because neither polypropylene or polyethylene is swollen in the solvents used for these reactions.

The oxidation of polypropylene and polyethylene was investigated using reagents that have been successful for C-H bond activation in small molecule systems. Changes in the hydrophobicity of the surface was studied by looking at changes in the contact angle of water on these surfaces. The depth of reaction and the type and degree of functionalization was investigated by ATR-IR, transmission IR, UV-VIS and XPS analysis. In addition, hydroxylated surfaces were labeled with halogenated acid chlorides for XPS analysis.

References

1. Dias, A. J.; McCarthy, T. J. *Macromolecules* **1984**, *17*, 2529.

2. Dias, A. J.; McCarthy, T. J. *Macromolecules* **1985**, *18*, 1826.

3. Dias, A. J.; McCarthy, T. J. *Macromolecules* **1987**, *20*, 2068.

4. Costello, C. A.; McCarthy, T. J. *Macromolecules* **1987**, *20*, 2819.

5. Costello, C. A.; McCarthy, T. J. *Macromolecules* **1984**, *17*, 2940.

6. Brennan, J. B.; McCarthy, T. J. *Polym. Preprints, ACS Div. Polym. Chem.* **1988**, *29(2)*, 336.

7. Bening, R. C.; McCarthy, T. J. *Polym. Preprints, ACS Div. Polym. Chem.* **1988**, *29(2)*, 338.

8. Lee, K. W.; McCarthy, T. J. *Macromolecules* **1988**, *21*, 2318.

9. Lee, K. W.; McCarthy, T. J. *Macromolecules* **1988**, *23*, 3353.

10. Shilov, A. E. The Activation of Saturated Hydrocarbons by Transition Metal Catalysts, D. Riedel Publishing Co., Dordrecht, 1984.

11. Sheldon, R. A.; Kochi, J. K. Metal-Catalyzed Oxidations of Organic Compounds, Academic Press, New York, 1981.

12. Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245.

13. Bergman, R. G. *Science* **1984**, *423*, 902.

14. Briggs, D. M.; Briggs, D. *Polymer* **1981**, *22*, 7.

15. Blais, P.; Carlsson, D. J.; Csullog, G.W.; Wiles, D.M. *J. Coll. Int. Sci.* **1974**, *47*, 636.

16. Rasmussen, J. R.; Stedronsky, E. R.; Whitesides, G.M. *J. Am. Chem. Soc.* **1977**, *99*, 4736.

17. Rasmussen, J. R.; Bergbreiter, D. E.; Whitesides, G.M. *J. Am. Chem. Soc.* **1977**, *99*, 4746.

18. Hanotier, J.; Camerman, M.; Hanotier-Bridoux, M.; de Radzitzky, P. *J. Chem. Soc. Perkin II* **1972**, 2247.

19. Groves, J. T.; Nemo, T .E. *J. Am. Chem. Soc.* **1983**, *105*, 6243.

20. Olah, G. A.; Parker, D. G.; Yoneda, N. *Angew. Chem. Int. Ed. Engl.* **1978.**

21. Deno, N. H.; Jedziniak, J.; Messer, L.; Meyer, M.; Stroud, S.; Tomezco, E. *Tetrahedron* **1977**, *33*, 2503.

22. Mazur, S. *Pure and Appl. Chem.* **1975**, *41*, 145.

23. Muller, W.; Schneider, H. J. *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 407.

24. Takaishi, N.; Fujikura, Y.; Inamoto, Y. *Synthesis* **1983**, 293.

25. Geletii,Y.V.; Zakharov, I.V.; Karasevich, E.I.; Shteinman, A. A. *Kinet. Katal.* **1981**, *22*, 349.

26. Geletii,Y.V.; Zakharov, I.V.; Karasevich, E.I.; Shteinman, A. A. *Kinet. Katal.* **1981**, *20*, 1124.

27. Karasevich, E.I.; Muradov, N.Z.; Shteinman, A. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1974**, *8*, 1805.

28. Mimoun, H.; de Roch, I.S.; *Tetrahedron* **1975**, *31*, 777.

29. Lavrushko, V.V.; Khenkin, A.M.; Shilov, A.E. *Kinet. Katal.* **1980**, *21*, 276.

30. Brandrup, J; Immergut, E.H. Polymer Handbook, Wiley Interscience, New York, 1975, IV-241.

31. Tsubokawa, N.; Fujiki, K.; Sone, Y. *J. Poly. Sci. Chem. Ed.* **1986**, *24*, 191.

32. Deno, N. C.; Messer, L. A. *Chem. Comm.* **1976**, 1051.

33. Deno, N. C.; Gladfelter, E. J.; Pohl, D. G. *J. Org. Chem.* **1979**, *44*, 3728.

34. Briggs, D; Kendall, C.R.; Blythe, A. R. *Polymer* **1983**, *24*, 47.

35. Nuzzo, R.E.; Smolinsky, G. *Macromolecules* **1984**, *17*, 1013

36. Citobicky, P.; Mikulasova, D.; Chrastova, V.; Mefzlik, J.; Majar, J. *Angew. Chem. Int. Ed. Engl.* **1983**, *117*, 131.

CHAPTER 5

EXPERIMENTAL

Materials and Methods

Materials

Heptafluorobutyryl chloride (HFBC), trifluoroacetic anhydride, BH_3 (1.0 M in THF) , *m*-chloroperbenzoic acid (MCPBA), $SnCl_2 \cdot 2H_2O$ and Sn^0 (powder, 325 mesh) were purchased from Aldrich and used without further purification. When used as reaction solvents, THF was distilled from sodium benzophenone dianion under nitrogen and used directly from the still and methanol was distilled from magnesium under nitrogen and stored in a teflon stopcock sealed storage flask. Washing solvents (THF, $MeCl_2$, MeOH) were reagent grade unless otherwise noted. House water was redistilled with a Gilmont still.

Polyethylene (PE): Three types of PE were used for these studies. Standard technical grade PE (SHPE) was used in the first few studies without further purification. Linear Low Density PE (LLDPE) was obtained as a gift from Dr. Roger Porter's group[1], and had originally been purchased from CdF Chemie (#B:FW1290, δ=0.92 g/mL, Mn=36,000 and 49% crystallinity). High density PE (HDPE) was purchased from Aldrich (18,190-0, T_m=130°C, melt index 0.25). Isotactic polypropylene (PP, 1 mil, 25 mil) was purchased from Hercules.

Glassware

Reaction tubes with o-ring joints were used in these reactions to avoid the use of stopcock grease. A typical reaction tube and a condenser jacketed tube used for some reflux reactions are shown in Figure 5.1.

Analysis Methods

Dynamic contact angles were obtained as the average of at least five advancing and receding measurements on different areas of each film sample, using a Ramé-Hart telescopic contact goniometer and a Gilmont syringe with a 24-gauge flat-tipped needle. Water was used as the probe fluid for all measurements. Attenuated total reflectance (ATR-IR) infrared spectra were obtained under nitrogen from an IBM 38 FT IR with 4 cm^{-1} resolution, triangular apodization and a deuterated triglycine sulfate detector, using a germanium internal reflection element (45°).

X-ray photoelectron spectra (XPS) were obtained using a Perkin-Elmer Physical Electronics 5100 spectrometer with MgKα excitation (300 W, 15 KeV). Spectra were recorded at 15° and 75° from the surface and the reported binding energies were not corrected for charging. Atomic composition data and peak area calculations were determined using the instruments supplied software. UV-VIS spectra were recorded on a Perkin-Elmer Lambda 3A spectrophotometer. Gravimetric analysis was carried out using a Cahn 29 electrobalance containing a polonium source. Before weighing, each film sample was charge neutralized with a Zerostat (Aldrich).

Purification of HDPE, LLDPE

Both the LLDPE and the HDPE were redissolved and reprecipitated before being pressed into films (VI-52, 90). In a typical batch, PE (9.2 g) was added to 600 mL of p-xylene (1.5% w/v), along with 0.27 g of 2,6-di-*tert*-butyl-4-methylphenol (an oxidation

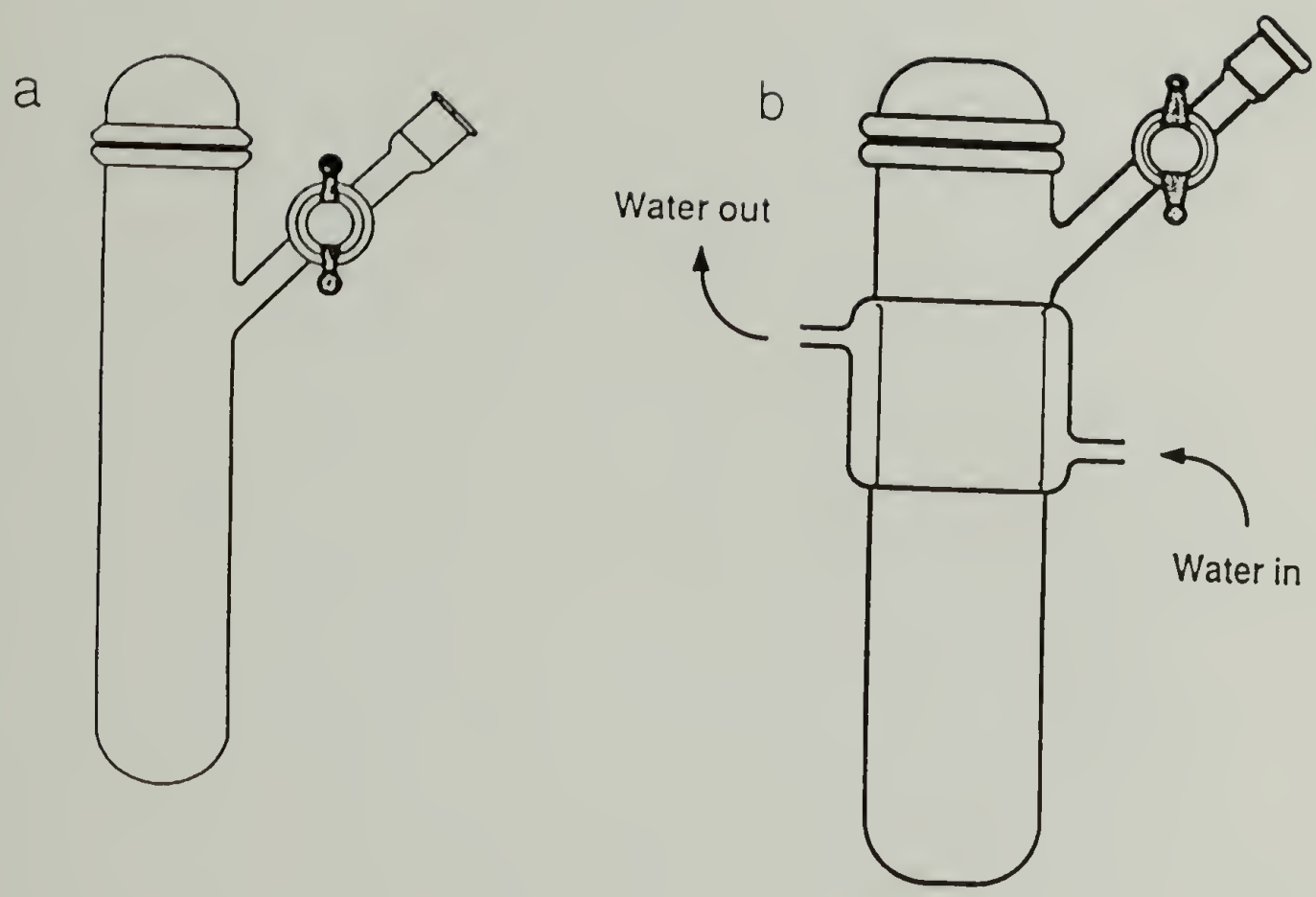


Figure 5.1. Reaction Tubes Used for Surface Reactions. a) Typical Schlenk Tube b) Condenser Jacketed Tube

inhibitor). The mixture was heated to reflux to insure complete solution of the PE, and then poured slowly into 2 L of cold technical grade MeOH. The solvent was filtered off using a buchner funnel and the fluffy white polymer was washed with 3 L of technical grade acetone before being dried for several days on the vacuum line. More concentrated solutions of LLDPE (5-8%) could be made up, but concentrations of HDPE greater than 2% resulted in large clumps of precipitated polymer from which it was difficult to remove all of the xylene.

Film Pressing

A Carver Press was used to press 0.1-0.2 mm films of freshly precipitated PE (VI-59, 90). Different thicknesses of Mylar "picture frames" functioned as spacers to regulate film thickness. One and two pieces of 5 mil Mylar typically produced 0.1 and 0.2 mm sheets of PE, respectively. After preheating the plattens to ~172°C, PE (1.3 g) was spread evenly in the center of a 10 x 12 cm window, using fresh pieces of Mylar and smooth brass plates on the top and bottom. The assembly was placed on the bottom platten and the top platten was lowered until contact with the upper mylar was achieved. The PE was allowed to melt for 10 min before being pressed using the following series of cycles: 10 x 1000 psi, 5 x 2000 psi, 5 x 5000 psi 5 x 8000 psi 3 x 10,000 psi. The films were held at 8-10,000 psi for 10 min and then dropped quickly into a bucket of ice water after releasing the pressure.

Standard Reaction Procedures

Preparation and storage. Prior to reactions, films were washed with 5 x $MeCl_2$, 5 x MeOH and 5 x THF and then refluxed in $MeCl_2$ for 30 min before a final rinse with 3 x $MeCl_2$. Films were stored on the vacuum line for at least 24 h before being used in surface studies. Films were stored and dried under vacuum, using the vacuum manifold pictured in Figure 2.3 Unless otherwise noted, vacuum line pressure was 0.02 mm.

Post-Reaction Washing. The reaction solvent was decanted, using a glass stirring rod to keep the films in the Schlenk tube. Reagent grade solvents and doubly distilled water were used for washing. These were added to the tubes in 20 mL portions, unless noted otherwise and the tubes were agitated using a Vortex Genie™. Each portion was decanted and the next added until the washing sequence was complete. The first solvent was generally the same as the reaction solvent unless the reagents were more soluble in another typical washing solvent, and $MeCl_2$ was usually the last solvent because it evaporated quickly.

Stirring. Stir bars were used as noted, depending on the relative densities and polarities of the film and the reaction solvent. If the films floated on the top of the reaction solvent, then stirring was used to keep them submerged, and the rate was adjusted to insure that the films would not touch the stir bar. If stirring was not practical and the films would not stay immersed, then nitrogen or oxygen was bubbled through the reaction to provide agitation.

meta-Chloroperbenzoic acid (MCPBA)

MCPBA Oxidation with Chloroform (VI-69): Meta-chloroperbenzoic acid (MCPBA) in chloroform (0.2 M, 20 mL) was added to each of 2 Schlenk tubes with condenser tops, along with several PE (LLD, HD) and PP films. A 13 mm glass rod was inserted into Tube A as shown in Figure 5.1 to keep the film immersed and the reaction mixture was sonicated. The water in the sonicator was 43°C during most of the reaction. A 10 mm stir bar was added to tube B and the tube was immersed in a 69°C oil bath to achieve reflux conditions. The reactions were drained using a pipet at the 12 h point and fresh solution (0.2 M MCPBA) was added. After 24 h, the films were removed and washed with 5 x $MeCl_2$, 5 x MeOH, 5 x H_2O and 2 x MeOH before being placed in a

soxhlet extractor with MeOH overnight. They were rinsed with 2 x $MeCl_2$ and dried under vacuum.

MCPBA Oxidation with Dichloroethane (VI-71): A second oxidation of PE and PP was run using the same procedure described above for VI-69, with dichloroethane as the solvent. The sonication bath was 45-49°C and the oil bath was 71-75°C during the reactions. Both the sonicated and reflux reactions were run for 10.5 h. Washing conditions were equivalent to those described for VI-69.

Benzoyl Peroxide /Alcohol (BPO/ROH)

Specific conditions for the different trials of the alcohol/benzoyl peroxide (ROH/BPO) reaction (VI- 6, 8, 10, 37) are found in Table 5.1. The procedure described below for VI-6 was followed unless noted otherwise for each of the BPO/ROH reactions. Reaction VI-6 compared methanol (MeOH) and isopropanol (i-PrOH) as reaction solvents, and subsequent reactions were restricted to MeOH.

Table 5.1. Reaction Conditions for BPO/ROH Reactions.

Reaction	Major system Variable	Amt. BPO	Amt. ROH	Control	Oil Bath Temp	Time
6A	solvent	0.52g	20 mL	None	48°C	27.5h
6B	solvent	0.53	20 mL			
9	PP vs PE	0.55g	20 mL	MeOH (no BPO)	78°C, reflux	20h
11	PP vs PE	0.55g	20 mL	MeOH (no BPO)	78°C, reflux	20h
37	for XPS	.50	35 mL		78°C, reflux	24 h
65	for XPS	.50	35 mL		78°C, reflux	24 h

BPO/ROH with Methanol and Isopropanol (VI-6): Samples of PP and PE were placed in each of two standard reaction tubes equipped with condenser jackets. BPO (0.52 and 0.53 g, respectively) was added to each of the tubes followed by 20 mL of methanol and i-PrOH. The reaction mixtures were blanketed with nitrogen and the tubes were placed in an oil bath (48°C) for 27.5 h. Not all of the BPO dissolved during this process and some remained even after 27.5 h. The films were washed with 1 x ROH and 2 x $MeCl_2$ under nitrogen, followed by 5 x $MeCl_2$ in air, before being placed under vacuum. Reactions VI- 8, 10, 37 were washed with 10 x $MeCl_2$ in air, instead of rinsing with alcohol first. VI-64 run for 24 h.

Stannous Chloride/Oxygen Oxidation of PE and PP

The complete set of reaction conditions for the stannous chloride/oxygen ($SnCl_2/O_2$) autoxidation of PE and PP (VI-13, 17, 21, 21, 23, 27, 39, 30, 34, 46, 50, 54, 62, 66, 74) are detailed in Notebook VII.. Deviations from the standard procedure described in this section are specified below by notebook page number. Solvent (20 mL of 1.5 M H_2O in acetonitrile) was added to a schlenk tube containing the appropriate amounts of $SnCl_2 \cdot 2H_2O$. Sn^0 was added at this time to some reactions as an additional reducing agent. PP and PE films were added and the tubes were capped with rubber septa. Oxygen was bubbled through the solution using stainless steel cannula for reactions (VI-13, 17, 21, 21, 23, 27) and 1/8" polypropylene cannula for all subsequent $SnCl_2/O_2$ reactions. Additional solvent was added to some reactions if low solvent levels interfered with good mixing conditions. After 2-12 hours, the films were removed and washed with 3 x MeOH, 3 x H_2O, 3 x MeOH and 3 x $MeCl_2$. Films were dried under vacuum (0.02 mm) for a minimum of 12 h before analysis. The reactions were typically

exothermic during the initial mixing period and the solutions remained slightly cloudy and yellow to green colored at concentrations greater than 0.3 M $SnCl_2$.

$SnCl_2/O_2$ Survey Reaction (VI-13): A preliminary survey of the $SnCl_2/O_2$ reaction was run in 25 mL round bottomed 14/20 flasks to examine the effect of different reaction solvents. The following solvent systems were studied:

VI-13 A: 0.1 M. $SnCl_2$ / 1.5 M H_2O

VI-13 B 0.1 M. $SnCl_2$ / 1.5 M H_2O / CH_3CN

VI-13 C 0.1 M. $SnCl_2$ / 1.5 M H_2O / CH_3CN / 0.1 M. HCl

VI-13 D CH_3CN

$SnCl_2/O_2$ Reaction / Reflux Conditions (VI-30): The standard $SnCl_2/O_2$ reaction protocol described above was run under reflux conditions, resulting in dark yellow colored solutions after 2 h. Films were taken out at intervals (1, 2, 4, 8, 22 h) to look at differences in reaction depth over time. The presence of tin on the XPS spectra of previous reactions prompted the investigation of several types of washing conditions. The films from this reaction were extracted in a 250 mL beaker with refluxing MeOH before being washed with the standard protocol (3 x MeOH, 3 x H_2O, 3 x MeOH and 3 x $MeCl_2$). As detailed in Table XX, and on VI-31, some of the films were further washed by stirring in 10% NaOH or by soxhlet extraction with MeOH.

$SnCl_2/O_2$ Reaction using a 10% Water/Acetonitrile Post-Wash (VI-46): After using the standard reaction protocol, samples from this reaction were washed with 10 x 10% H_2O/CH_3CN, 5 x MeOH and 3 x $MeCl_2$. Some of these films were further washed by stirring in 10% NaOH or by soxhlet extraction with MeOH.

$SnCl_2/O_2$ Reaction with Prolonged Post-Washing Cycle (VI-51): Films from this reaction were also washed with 10 x H_2O/CH_3CN, 5 x MeOH and 3 x $MeCl_2$. They

were then stirred for 72 h in one of the following: 10% H_2O/CH_3CN (51-A), 5% NaOH (51-B) and 0.1 N HCl (51-C). The final rinse was 3 x MeOH and 3 x $MeCl_2$.

$SnCl_2/O_2$ Reaction/ Soxhlet Extraction Post-Wash (VI-54): Films were washed with 10 x H_2O/CH_3CN before being extracted in a soxhlet extractor with MeOH for 12 h. They were then rinsed with 3 x MeOH and 3 x $MeCl_2$, before being exposed to more rigorous washing conditions, as detailed below.

$SnCl_2/O_2$ Reaction with Extreme Post-Wash Conditions (VI-57): Samples from VI-54 were treated with HCl (conc), 10 M KOH, 2 M NaSH (in 50/50 $MeOH/H_2O$) and 10% H_2O/CH_3CN in order to remove tin salts from the surfaces. Some of the tubes containing the washing reagents (~40 mL) and films were sonicated, while others were bubbled with nitrogen to insure adequate coverage and mixing. The sonicated extractions were carried out in short 28/34 reaction tubes, and #13 hollow glass rods were used to keep the films upright and immersed in the solvent. The reflux reactions were done in schlenk tubes with condenser jackets built into the upper half of the tube, as shown in Figure 5.1. Control samples (unreacted PP, PE) were added to each of these tubes to look at the effect of these severe washing conditions on virgin films. The samples from VI-54 were extracted for 12 h, and the control samples were extracted for 7 h. Films extracted in acid were neutralized by rinsing with base after washing once with H_2O, and vice versa. All films were rinsed after treatment with 10 x H_2O, 5 x MeOH and 5 x $MeCl_2$.

$SnCl_2/O_2$ Reaction with 2 M KOH Post-Wash (VI-62): PP and PE films (10 each) were reacted under standard conditions (0.75 M $SnCl_2$ and Sn^0, 1.5 M H_2O) for a repeat of the base extraction. The films were washed immediately after the reaction with 5 x 10% H_2O/CH_3CN, 5 x MeOH and 3 x $MeCl_2$ and then sonicated in 2 M KOH for

13 h. They were then washed with 1 x 0.1 N HCl, 12 x H_2O, 5 x MeOH, and 5 x $MeCl_2$ and placed under vacuum.

$SnCl_2/O_2$ Reaction (0.10 M $SnCl_2$ and Sn^0, 1.5 M H_2O) (VI-67): PP and PE films were reacted using the standard procedure under more dilute conditions (with 0.10 M $SnCl_2$ and Sn^0, 1.5 M H_2O) and washed with 5 x 10% H_2O/CH_3CN, 5 x MeOH and 3 x $MeCl_2$. The reacted films plus some virgin PP and PE control samples were sonicated in 2 M KOH for 9 h, soaked overnight in 2M KOH, washed with 5 x H_2O and sonicated in 0.1 N HCl for 2.5 h. They were then washed with 5 x 0.1 N HCl, 12 x H_2O, 5 x MeOH and 5 x $MeCl_2$ and placed under vacuum.

$FeCl_2/O_2$ Reaction (VI-25): The effects of using $FeCl_2 \cdot 4H_2O$ as the oxidant were examined for both acetone and acetonitrile solvent systems, using the same reaction configuration described for the $SnCl_2/O_2$ system. These reactions were also 0.1 M in 1,4--phenylenediamine and benzoic acid. The films were washed with 3 x MeOH, 3 x H_2O, 3 x MeOH and 3 x $MeCl_2$ and extracted for 4 h in a soxhlet extractor with MeOH.

Trifluoroperacetic Acid (TFPAA)

The oxidation of PE and PP was carried out with TFPAA using a variety of reaction times and reagent concentrations and temperatures (VI-43, 49, 72, 76, 78, 80, 95, 109, 113). Reactions VI-42, 49 and 80 were run under a blanket of nitrogen. All other were run in closed tubes with polypropylene outlet needles venting to the atmosphere.

TFPAA / Room Temperature (VI-42): PP and PE films were placed in a #20 diameter tube with a 0.5" egg-shaped stir bar. Trifluoroacetic acid (20 mL) and 30% H_2O_2 (1.1 mL) were added slowly via graduated cylinder and syringe, respectively, while

swirling the tube to insure good mixing. The air space in the tube was flushed with nitrogen. Both the PP and the PE films were less dense than the TFPAA solution, and the stirring rate was adjusted such that the films were caught in the top part of the vortex in order to keep the films submerged throughout the reaction. Care was taken to keep the stirring rate such that the films did not come in contact with the stir bar. These films were reacted for 12 h. They were soaked in H_2O for 8 h and washed with 2 x H_2O, 5 x $NaHCO_3$, 5 x H_2O, 3 x MeOH, 3 x $MeCl_2$.

TFPAA / Reflux with a Trifluoroacetic Acid Control(VI-72): PP and PE films were combined with TFA (20 mL) and H_2O_2 (1.1 mL) in two separate reaction tubes. The first tube was sonicated and the second was reacted at reflux (84°C) for 8.5 h. The reaction mixture was drained via pipet, fresh solution was added, and the films were allowed to react for another 11.5 h. The films were washed with 2 x H_2O, 5 x $NaHCO_3$, 5 x H_2O, 3 x MeOH, 3 x $MeCl_2$ and extracted in MeOH in a soxhlet extractor for 14 hours. Control samples (VI-72 C, D) were reacted under the same conditions without adding H_2O_2 to the tubes.

TFPAA / Reflux / Soxhlet Extractor Post-Wash (VI-76): PE and PP films were reacted for 20 h at reflux, followed by washing with 10 x MeOH and 5 x $MeCl_2$ and soxhlet extraction in MeOH for 9 h.

TFPAA / Reflux with [H_2O_2] x 1 and [H_2O_2] x 2 (VI-78): PE and PP films were reacted for 12 h at reflux using 1.1 and 2.2 mL of H_2O_2, respectively, followed by washing with 10 x MeOH and 5 x $MeCl_2$ and soxhlet extraction in MeOH for 9 h.

TFPAA / Reflux with [H_2O_2] x 1 and [H_2O_2] x 2 (VI-80): PE and PP films were reacted for 8.5 and 20 h at reflux using 1.1 and 2.2 mL of H_2O_2, respectively, followed by washing with 10 x MeOH and 5 x $MeCl_2$ and soxhlet extraction in MeOH for 9 h.

Examination of the Rate of the TFPAA Reaction

The TFPAA reaction was examined as function of time by reacting samples in refluxing TFPAA for 1, 3, 6, 12 and 24 h. A 24 h control was also run, using trifluoroacetic acid without any H_2O_2. Enough film samples were run such that data points could be acquired for each reaction time for XPS, ATR, UV-Vis, contact angle and gravimetric analysis. Gravimetric samples were stored under vacuum until they reached constant weight for 3 days in a row after the initial film washing. They were also weighed after reaction and post washing, until constant weight had been attained. The thinnest films were chosen as UV samples and each was checked to insure positive absorbances with respect to the reference film. These were measured against the same reference piece of film both before and after reaction to record the change in absorbance vs. reaction time. Sample dimensions for all of the analysis procedures are shown in Table 5.2.

Table 5.2. Film Sample Dimensions.;

Sample Type	Length (cm)	Width (cm)	Thickness (cm)
XPS	1.5	2.0	0.02 - 0.03
ATR	1.2	2.2	0.01 - 0.02
Contact Angle	1.3	1.8	0.01 - 0.02
UV-VIS	1.2	2.2	0.01 - 0.02
Gravimetric (2)	1.5	1.5	0.02 - 0.03

TFPAA / 24 Hour Series. (VI-95) Reactions with TFPAA were run under the standard reflux conditions described above (VI-78, 80) using 1.1 mL of H_2O_2 in 20 mL of TFA and PE cannula tubing for transfers. Films were transferred into degassed MeOH to stop the reaction and the films were washed with 10 x MeOH and 10 x $MeCl_2$ before being extracted for 8 h in a soxhlet extractor with $MeCl_2$.

TFPAA / 1 Hour Series. When XPS and ATR results showed that considerable reaction had taken place in the first hour, a set of 15, 30 and 45 min samples (VI-109) were run under identical conditions, except that the TFPAA solution was brought to a boil before adding the films. The TFPAA was removed via PE cannula and degassed MeOH was added to each tube after the appropriate reaction time. Films were rinsed immediately with 2 x MeOH and then soaked in MeOH for 0.5 h. They were then washed (10 x MeOH, 10 x $MeCl_2$) before being place in a soxhlet extractor with $MeCl_2$ for 8 h.

TFPAA / 0.25 Hour Series. Several films (VI-113) were reacted using the short term reaction procedure (VI-109) to prepare substrate films for derivatization.

Derivatization of Oxidized Surfaces

Hydrolysis of VI-PE-[O]-TFA Surfaces. (VI-83, 104, 115): For Reaction VI-115, a graduated cylinder containing 2.0 g of NaOH was sealed with a rubber septum and flushed with nitrogen. Distilled water which had been purged with nitrogen to remove the oxygen was added via cannula to make 100 mL of 0.5 M NaOH. This solution was added via cannula to two #25 o-ring tubes, equipped with stir bars and built-in condensers. The tubes contained 5 PE-[O]-TFA films from VI-113 (0.25 h reaction) plus virgin HDPE films as control samples. The tubes were evacuated and filled with nitrogen 3 times before 20 mL of the 1.0 M NaOH solution was added to each via cannula. The tubes were immersed in a 61°C oil bath and the films were reacted for 8 h. Films were washed with 5 x H_2O, 5 x 0.1 N HCl, 10 x H_2O, 5 x MeOH, 5 x $MeCl_2$. VI-83 was run at 65°C for 7.8 h, using 1.0 M NaOH. VI-104 was run at 42°C for 12 h, using 0.1 M NaOH. Washing procedures for both were identical to those described for VI-115.

Borane/THF Reduction of PE-[O]-TFA Surfaces. (VI-111, 117): For Reaction VI-111, samples from VI-95E (3 h reaction with TFPAA) were placed in a #20 o-ring tube with a small stir bar, and the tube was flushed thoroughly with nitrogen. Freshly distilled THF (20 mL) was added via cannula, and 2.0 mL of 1.0M BH_3/THF was added via syringe over 2 min. Films sank to the bottom of the tube, and no stirring was necessary. After 13 h, the reaction solution was removed via cannula and the films were washed with 4 x THF (dry, distilled) under nitrogen. After equilibrating separately in an ice bath, 10 mL of 30% H_2O_2 and 20 ml of 6% NaOH (degassed) were combined and added to the reaction tube. The films floated on the top of the basic peroxide solution, and a high stirring rate was necessary to keep the larger film samples submerged. After 9 hours at O°C, the reaction solution was removed via cannula and the films were washed with 3 x 6% NaOH, 5 x H_2O, 5 x 0.1*N* HCl, 10 x H_2O, 5 x MeOH and 5 x $MeCl_2$, before being placed on the vacuum line.

VI-117: The same procedure was followed as VI-111, except that the films were exposed to borane for 12 h and to basic peroxide for 8.5 h. The films were kept under nitrogen until after the first wash with 0.1 N HCl. Washing continued with 4 x 0.1 N HCl, 10 x H_2O, 5 x MeOH and 5 x $MeCl_2$, before placing the films on the vacuum line.

XPS Labeling Reactions for Surface Functional Groups. Labeling Reactions with Heptafluorobutyryl Chloride (HFBC) and Trifluoroacetic Anhydride (VI-85, 87, 89, 120) were carried out:

VI-120: Under nitrogen, HFBC (1.0 mL) and dry pyridine (0.4 mL) were added to 20 mL of dry THF and transferred via cannula to a Schlenk tube containing films from VI-113,115, 117. The films were reacted without stirring for 12 h. They were then washed with 10 x THF (under N_2), 10 x MeOH, 5 x $MeCl_2$. Labeling reactions VI-87

and 89 were run the same conditions using films from VI-78, and 80 for VI-87 and films from VI-66 ($SnCl_2/O_2$ reaction) for VI-89.

VI-85: The procedure for HFBC described above was followed using trifluoroacetic anhydride without any pyridine to label $SnCl_2/O_2$ reaction films from VI-74 A, B.

References

1. Benelhadjsaid, C. *J. Applied Polym. Sci.* **1985**, *30*, 741.

CHAPTER 6

DISCUSSION

Carbon Hydrogen Bond Activation at Hydrocarbon Polymer Surfaces

Our goal for this part of the dissertation research was to apply traditional carbon-hydrogen bond activation chemistry to saturated hydrocarbon polymers, specifically polyethylene (PE) and polypropylene (PP). We wanted to selectively functionalize these materials, such that we created a two dimensional array of functional groups which would address some of the interface problems associated with these polymers such as adhesion and wetting. Previously in our group, our job in limiting the number of types of products was facilitated by the chemical resistivity of the fluoropolymers that we had chosen to investigate for this same reason.[1-7]

For hydrocarbon substrates, this task is more difficult, because these polymers are more reactive, and the initial products are more reactive than the substrates in the case of oxidation. Even in solution reactions, highly selective functionalization of non-activated C-H bonds in paraffins is known for a few biological and enzymatic processes,[8] but is rarely seen for organic reactions. Some of the more recently studied alkane oxidation reactions[9-10] include N-oxides,[11] oxygen,[12] hydroxy radicals,[13] peroxides,[14] ozone,[15] and porphyrin 450 models.[16-17] Conditions for the surface modification of PE and PP have traditionally been harsh, to say the least, in order to compensate for the restrictions imposed by the heterogeneity inherent to reactions at a surface.[18-21] Although polymers or macromolecules do have certain unique properties, in terms of chemical reactions, they should share many of the same characteristics of organic small molecules. Instead of considering PE and PP as macromolecular monsters which need to be approached with big

sticks, we saw no reason to treat them differently than any other ordinary organic creatures. We wanted to show that bigger molecules do not necessarily mean bigger hammers.

With that in mind, we selected a group of reagents which were reported to selectively oxidize low molecular weight alkanes, specifically stannous chloride, *meta*-chloroperbenzoic acid, benzoyl peroxide and trifluoroperacetic acid. These were chosen on the basis of their potential to selectively place hydroxyl groups on the surface of PE and PP. As described in the following pages, we surveyed all of these reactions with both PE and PP, and then concentrated on the trifluoroperacetic acid system to look at the depth of reaction and nature of the products over time.

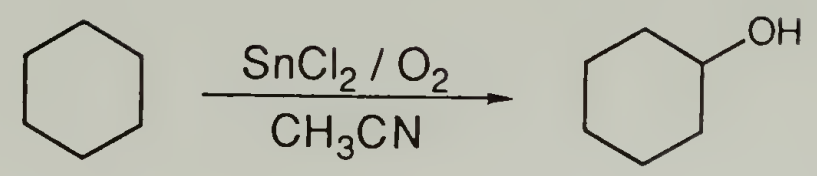
We analyzed the products from these reactions with a combination of techniques. XPS gave us an idea of the chemical composition of the surface, contact angle indicated changes in surface hydrophilicity and roughness and ATR-IR provided functional group information. We also used gravimetric analysis to look at the depth of the reaction to give us an idea of the number of groups being modified. The combination of all of these methods leads to an effective diagnosis of the situation at a modified surface, because each of these techniques has a different and complementary surface selectivity or depth from which it provides information.

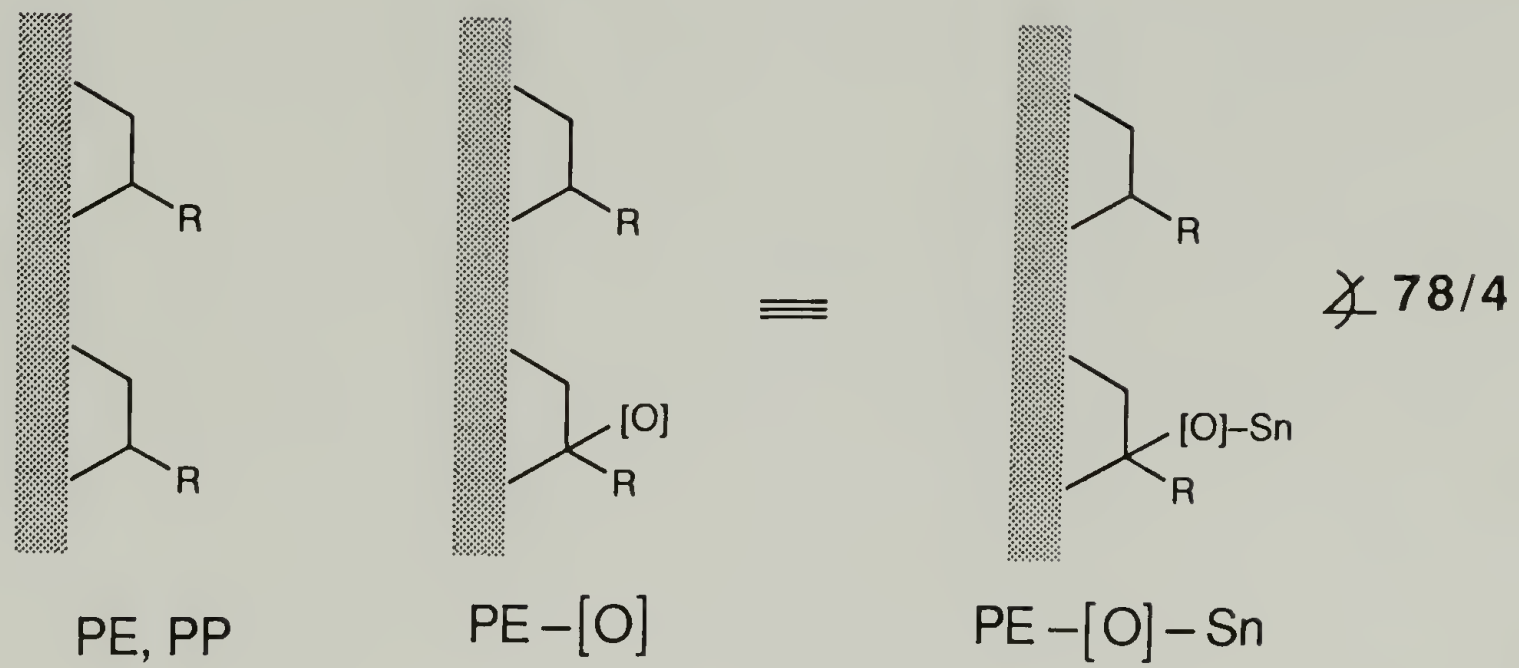
Several types of PE were used, including technical grade PE, linear low density PE (LLDPE) and high density PE (HDPE). The type of PE was specified in this discussion, if we are only referring to one type, but a generic PE label was applied in most cases because we did not do enough experiments to discern differences in behavior between the three.

Stannous Chloride Oxidation of PE and PP

The $SnCl_2/O_2$ oxidation system has been successfully used for oxidation of hydrocarbons to alcohols, as shown in Scheme 6.1 for cyclohexane. The reaction solvent was typically a mixture of water and acetonitrile. This system was thought to be a promising method for the hydroxylation of PE and PP films because the cyclohexane results suggested that the alcohols produced would not be further oxidized to ketones or acids, even when the reagents were in excess as is the case for reactions at surfaces.[22-27] Preliminary results based on contact angle measurements with this system were exciting. Using PE as an example, when elemental tin (Sn^0) was added as an additional reducing agent, contact angles of water (θ_A/θ_R) changed from 108/75 for virgin PE to 78/4, indicating a dramatic increase in the hydrophilicity of the surface. Further characterization using XPS showed large quantities of tin on the surface due to tin salts formed during the reaction which were not removed by rinsing with a standard progression of solvents (methanol, water, methanol and methylene chloride). The tin was probably present as an oxide species, which made it difficult to differentiate between surface oxygen associated with the tin and that incorporated as hydroxyl groups.

In light of the XPS results, reacted films were washed with copious amounts of either 0.1 N HCl, 0.1 N NaOH or 10%water/acetonitrile mixture, followed by a standard methanol, water, methanol and methylene chloride washing sequence. Significant amounts of tin remained in the XPS spectra, forcing an exhaustive investigation into different washing reagents, temperatures, times and stirring methods. Harsh washing conditions (10 M KOH or 12 M HCl) left only trace amounts of residual tin when the films were refluxed or sonicated, but control films (virgin PE, PP) incorporated up to 12% oxygen using these procedures. The most effective treatments were sonication for 12 h in



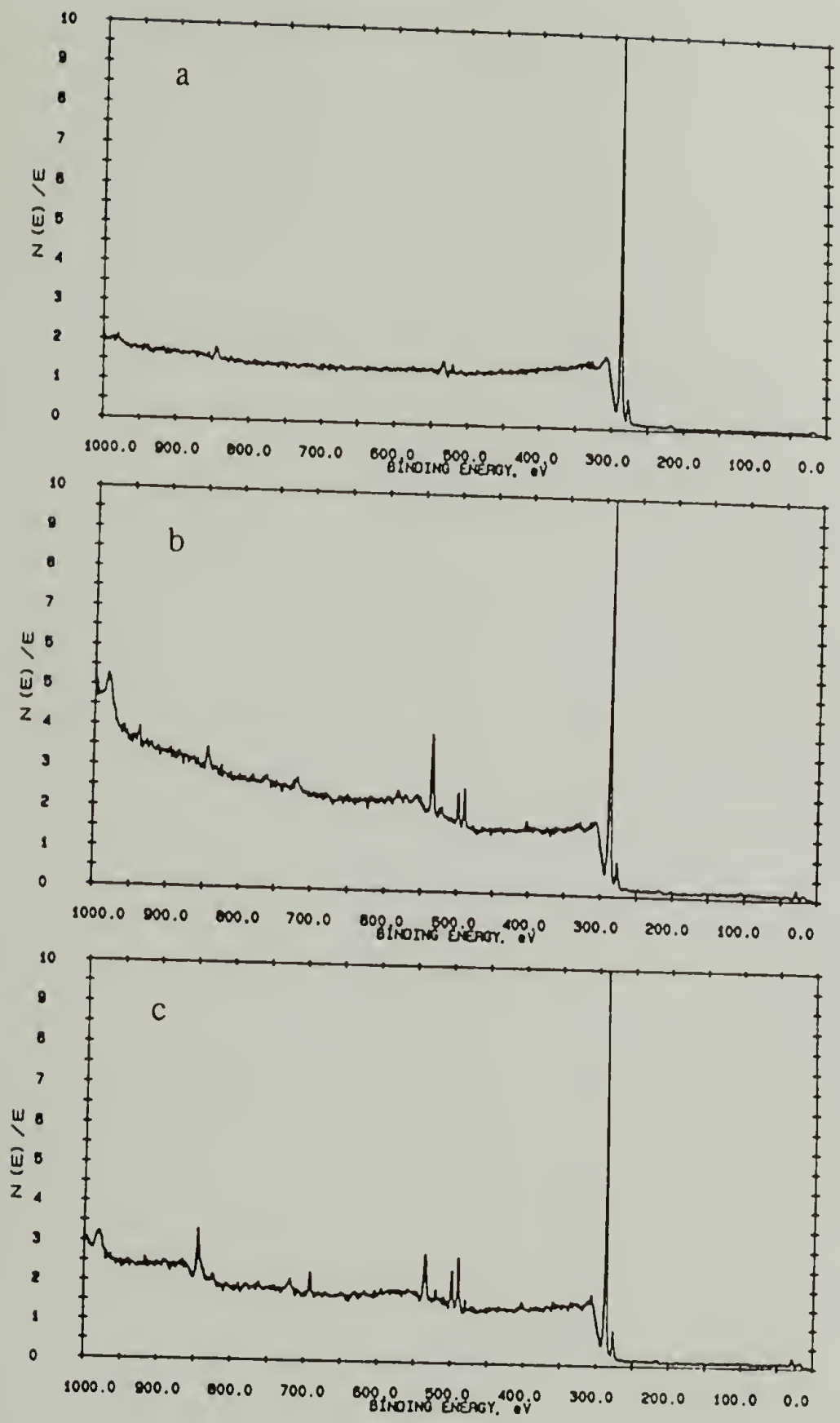


Scheme 6.1 Stannous Chloride/Oxygen Oxidation of Hydrocarbons as Applied to PE and PP.

2 M NaSH or 2 M NaOH, followed by the standard washing sequence, but these procedures resulted in the incorporation of up to 8% oxygen onto control films surfaces. These quantities were comparable to the amount of oxygen found on the films which had been reacted with $SnCl_2/O_2$.

Different reaction conditions were investigated concurrently with the washing studies to look at the effects of reacting PP and PE with different solvent systems (acetonitrile vs. acetone and different mixtures of H_2O and acetonitrile) as well as the effects of reaction time, temperature and the use of Sn° as an additional reducing agent. The presence of variable amounts of tin on these surfaces made it difficult to determine the effects of the different reaction variables on the number of hydroxyl groups added to the surface. Furthermore, we could not differentiate under these conditions between the oxygen incorporated as a result of the stannous chloride reaction and that which resulted from the washing procedures.

Despite these disadvantages, we attempted to label several of the reacted films with trifluoroacetic anhydride and heptafluorobutyryl chloride (HFBC). Typical XPS spectra for virgin PE films, PE reacted with $SnCl_2/O_2$ and a sample which had been labeled with with trifluoroacetic anhydride are shown in Figure 6.1. We have used trifluoroacetic anhydride and HFBC extensively for XPS labeling studies in our laboratory.[1-5,28] In our experience, Figure 6.1 indicates that very few, if any, surface hydroxyl groups were available for labeling. ATR-IR spectra for the virgin and $SnCl_2/O_2$ reacted films are shown in Figure 6.2. Given the limited extent of reaction evidenced by XPS and labeling studies, and the fact that hydroxyl groups were the only product groups that we had expected, it was not surprising that we saw only unmodified PE within the ATR sampling depth (.22 μ for PE at 3000 cm^{-1} with a 45° Germanium crystal).[29]



XPS Survey Spectrum (15°)

Virgin Polyethylene

Atomic Composition

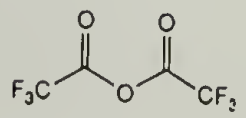
Carbon	99.59
Oxygen	0.41

$SnCl_2/O_2$

XPS Survey Spectrum (15°)

Atomic Composition

Carbon	88.88
Oxygen	8.85
Tin	0.66
Nitrogen	1.62

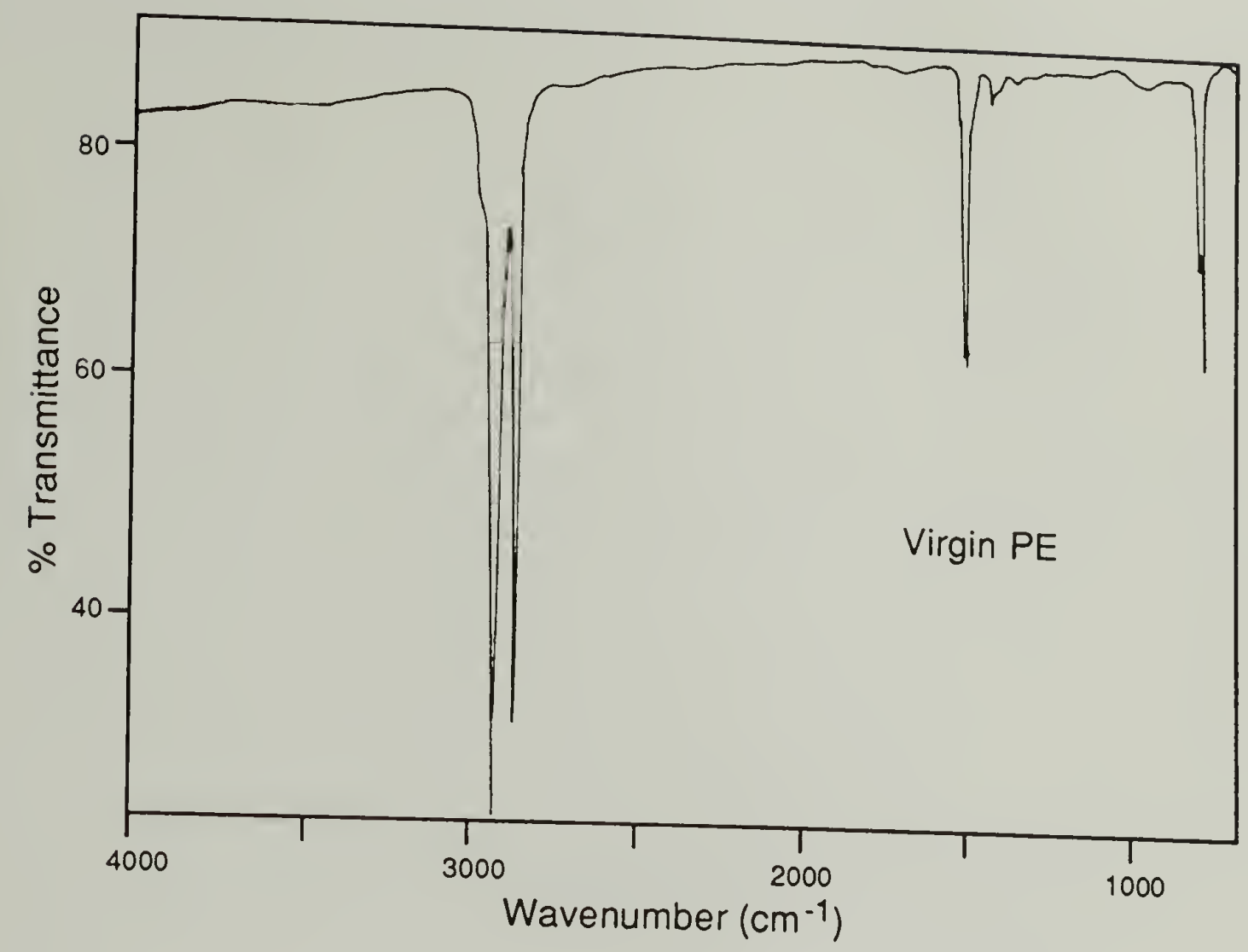


XPS Survey Spectrum (15°)

Atomic Composition

Carbon	95.36
Oxygen	2.92
Tin	0.57
Fluorine	0.83
Chlorine	0.83

Figure 6.1. XPS Spectra for Stannous Chloride/Oxygen Oxidation of PE. a) Virgin Film b) After Reaction with $SnCl_2$ c) After Labeling with Trifluoroacetic Anhydride



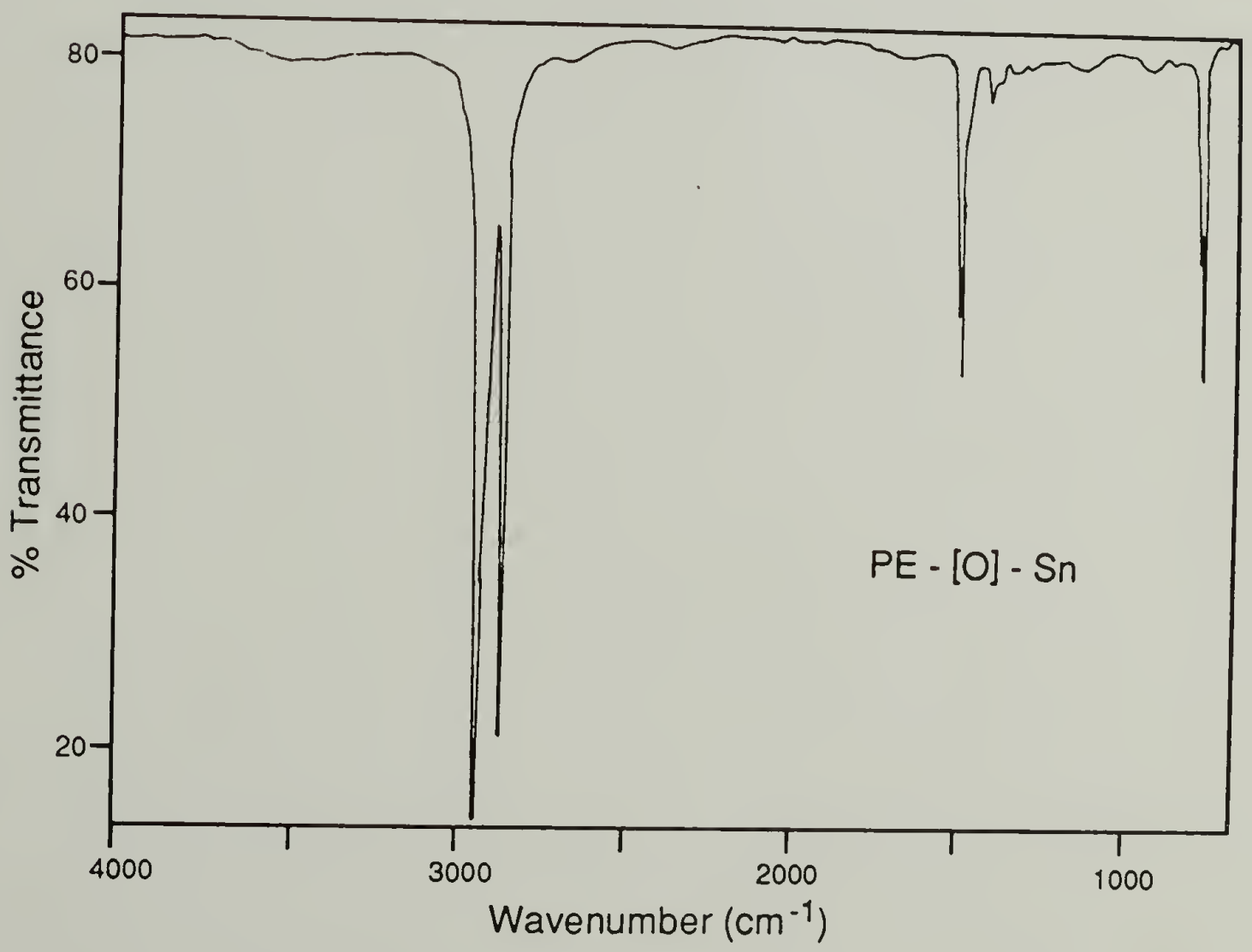


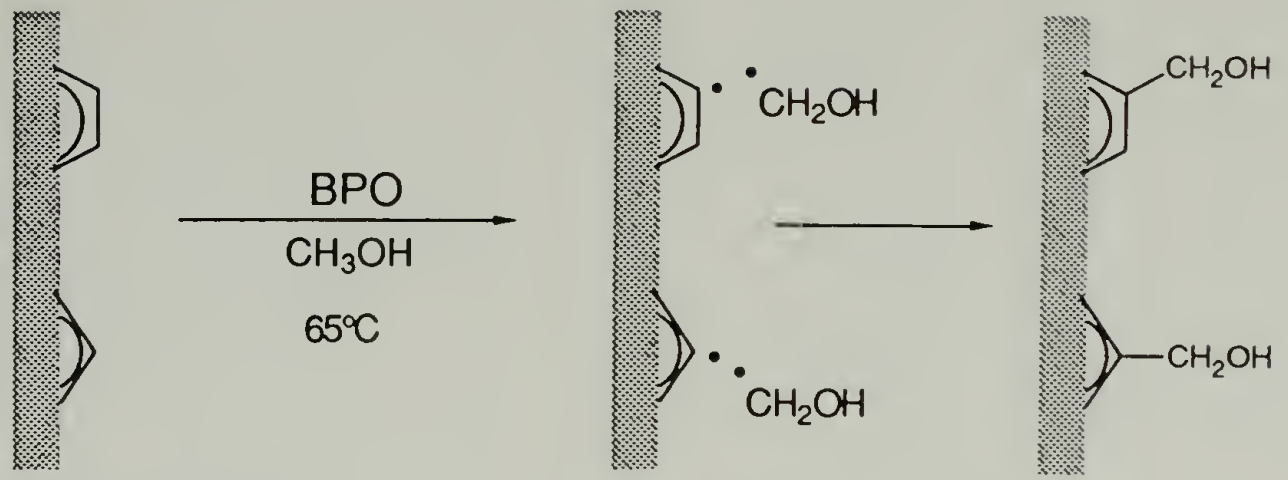
Figure 6.2. ATR-IR Spectra for Stannous Chloride Oxidized and Virgin PE Films.

Reaction of PE and PP surfaces with $SnCl_2/O_2$ produced a hydrophillic surface with a definitive change in chemical surface composition, as evidenced by changes in contact angle and XPS. The difficulties encountered in removing the tin salts from the reacted films made it difficult to differentiate between mechanisms of oxygen incorporation onto the surface, i.e. hydroxylation vs. tin salt adsorption. As a result, we did not pursue this type of oxidation for the surface selective modification of PE and PP.

Benzoyl Peroxide-Alcohol Oxidation of PE and PP

The successful application of the benzoyl peroxide-alcohol (BPO/ROH) system to carbon fibers made it very attractive for our purposes.[30] The reaction produces primary instead of secondary alcohols on PE and PP surfaces; hydroxyl groups attached to a surface by methylene spacer groups are ideal for further functionalization because the added degree of freedom provided by primary as opposed to secondary hydroxyl groups can facilitate reaction with electrophiles. As shown in Scheme 6.2, the benzoyl peroxide reacts with methanol to form methanol radicals and also abstracts hydrogens from the substrate. When the substrate is a polyolefin, the combination of these two species should result in the placement of primary alcohols on the surface.

Reaction with benzoyl peroxide in refluxing methanol fro 24 h resulted surfaces with definitive contact angle changes. For example, a PP film changed from 108/75 to 94/56 under these conditions. This result in itself was promising, and further investigation using XPS showed that 3% oxygen had been incorporated. Repeated attempts to place hydroxyl groups on the surface of PE and PP with the benzoyl peroxide-alcohol system resulted in the incorporation of a maximum of 3% oxygen, based on observations by XPS. Our first guess was that the hydrophilic methanol radicals may have not been able to achieve the physical proximity necessary to couple with radicals on the surface. Two



Scheme 6.2. Benzoyl Peroxide/Methanol Reaction with Hydrocarbon Substrates.

solutions were obvious: We could use a solvent which would wet PE better, or we could start with a more hydrophilic surface. To address the latter alternative, some of the films which had been reacted with $SnCl_2/O_2$ system were reacted again with BPO/MeOH, along with virgin PE and PP films. The previously reacted films showed the presence of tin and oxygen on the surface via XPS before reaction. Both sets of films showed very high oxygen by XPS (~20%), but both also showed the presence of high concentrations of tin, because they had been washed in the same tube as some other $SnCl_2$ reaction films. Although the large percentages of oxygen present were encouraging, the presence of the additional tin salts on both sets of films made these results difficult to interpret.

Using a less polar solvent such as decanol addressed the need to minimize the difference between the surface and solvent polarities, but this approach added several degrees of complexity to a reaction whose main appeal had been its simplicity with respect to mechanism and product distribution. Several types of radical species can be formed by hydrogen abstraction from decanol, and a variety of products might be formed by the addition of these species to the surface. In addition, the secondary radicals formed from decanol would be more hindered than the methanol radical and less likely to couple with surface radicals.

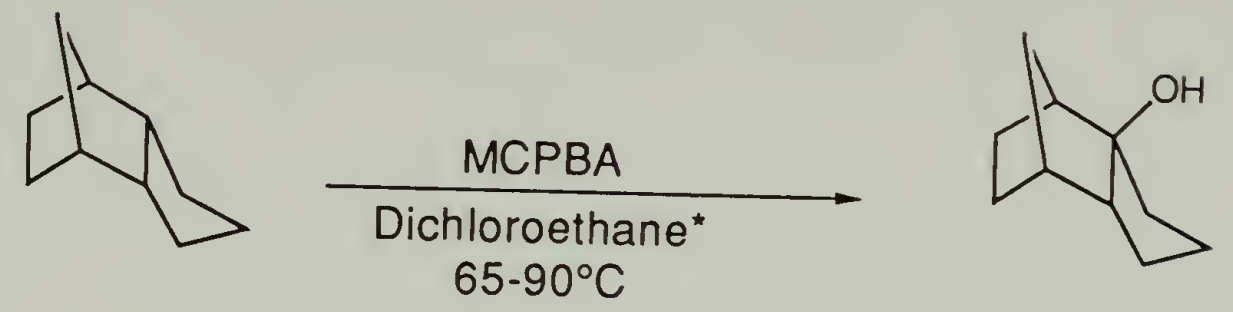
In light of the drawbacks inherent to using other alcohols, we returned to our original set of reaction conditions (refluxing methanol with 0.5 g BPO for 24 h). A final set of reactions using virgin PE and PP films showed only the previously seen 3%incorporation of oxygen. The most obvious problem with the application of this oxidation system was that we were trying to affect a reaction between two very unlike materials, with respect to hydrophobicity. Without the added organic character of acetonitrile as a cosolvent in the $SnCl_2/O_2$ system, the methanol radical may not have been able to get in close enough contact to the hydrophobic polymer films in order to affect a reaction.

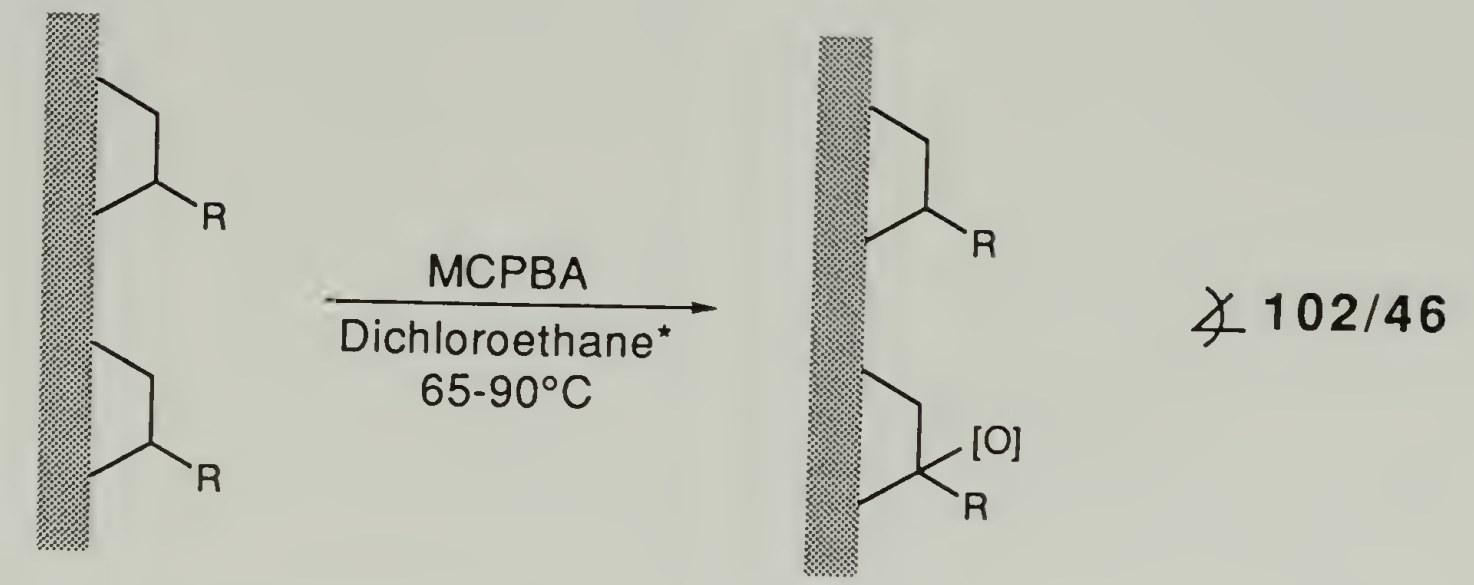
meta-Chloroperbenzoic Acid Oxidation of PE and PP

m-Chloroperbenzoic acid (MCPBA) has been used quite effectively for the hydroxylation of bridgehead carbon atoms, as shown in Scheme 6.3.[31-32] Following the solution protocol, PP, LLDPE and HDPE were reacted with MCPBA under reflux conditions with both methylene chloride and dichloroethane, as shown in Table 6.1. XPS results show that greater proportions of oxygen were incorporated onto the PP surfaces as opposed to both types of PE. The post reaction contact angle for the PE surfaces of 107/50 indicated that the surface energy had increased and although. contact angles were more difficult to measure on the PP films because of increased surface roughness, there was clearly a difference in both hydrocarbon surfaces following reaction with MCPBA.

Based on the reports of bridgehead hydroxylation by this particular perbenzoic acid system, it was not surprising that PP was reacted to a greater extent, given that one third of the carbons in PP are tertiary atoms. With both PE and PP and with both methylene chloride and dichloroethane as solvents, the reacted films had a bleached and cracked appearance with white craters 1-2 mm in diameter, possibly due to solvent crazing. This physical distress was not evenly distributed over the surface of the films; it was sometimes more pronounced one end or one side of the films, indicating that macroscopic imperfections present on the film surfaces prior to reaction may have provided potential nucleation sites. PE and PP are both slightly soluble in chlorinated solvents,[33] and the films could be swollen enough at the temperatures employed here to make solvent induced crazing or crystallization possible.

A further complication involved the small quantities of chlorine indicated by XPS. Residual solvent may have remained trapped in the films, but we saw chlorine in the XPS spectra of films which had been stored under vacuum for several days. MCPBA may have reacted with the polymers via a radical mechanism involving recombination of chlorobenzene radicals with radicals present on the polymer surface, similar to the side





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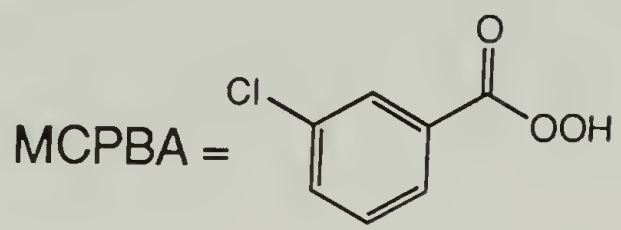
R = H (Polyethylene)

R = CH_3 (Polypropylene)

* Chloroform can be substituted



Scheme 6.3. MCPBA Hydroxylation of Bridgehead Carbon Atoms.

Table 6.1. MCPBA Oxidation of PP and HDPE, 24 h.

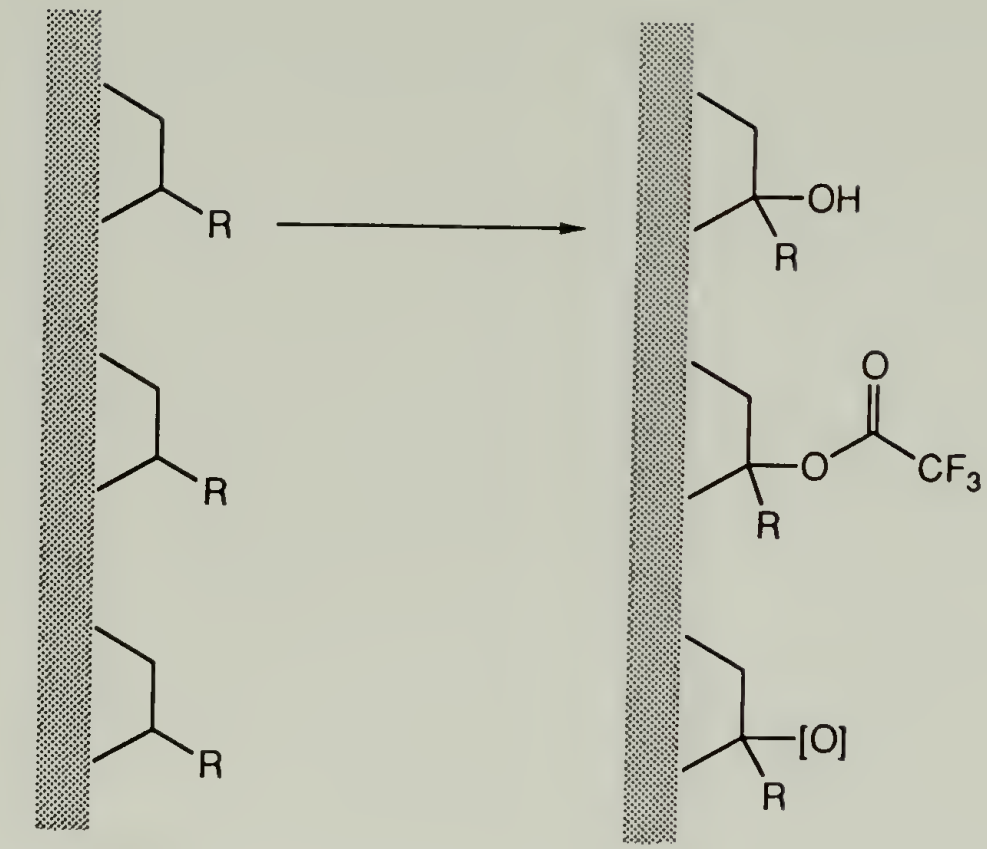
ESCA#	Sample#	Reaction Conditions	Polymer	Angle	S or M	C	O	Cl
783	68A	0.2M MCPBA/CHCl3, Sonicated 24 h	PP	15	S	100	1	0
785	68A	0.2M MCPBA/CHCl3, Sonicated 24 h	PP	75	M	100	2	0
799	68A	0.2M MCPBA/CHCl3, Sonicated 24 h	LDPE	15	M	100	2	0
801	68A	0.2M MCPBA/CHCl3, Sonicated 24 h	LDPE	75	M	100	2	0
759	68B	0.2M MCPBA/CHCl3, Refluxed 24 h	HDPE	15	M	100	3	1
761	68B	0.2M MCPBA/CHCl3, Refluxed 24 h	HDPE	75	M	100	2	1
729	68B	0.2M MCPBA/CHCl3, Refluxed 24 h	PP		M	100	7	1
731	68B	0.2M MCPBA/CHCl3, reflux 24(cont)	PP	75	M	100	3	1
756	70A	0.2M MCPBA/Dichloroethane Sonicated 24 h	PP	15	S	100	2	2
757	70A	0.2M MCPBA/Dichloroethane Sonicated 24 h	PP	75	S	100	3	3
767	70B	0.2M MCPBA/Dichloroethane Refluxed 24 h	HDPE	15	M	100	4	0
770	70B	0.2M MCPBA/Dichloroethane Refluxed 24 h	HDPE	75	M	100	2	0
753	70B	0.2M MCPBA/Dichloroethane Refluxed 24 h	PP	15	M	100	6	1
755	70B	0.2M MCPBA/Dichloroethane Refluxed 24 h	PP	75	M	100	3	0

reactions reported by Takaishi[31] when an excess of MCPBA was present. We have to assume that the reagents are always in excess for reactions at surfaces, placing this oxidation system at a distinct disadvantage with respect to producing a narrow distribution of products on a hydrocarbon surface.

Changes in contact angle and evidence of oxygen incorporation by XPS showed that this reagent was capable of affecting changes to the chemical surface composition of these hydrocarbon polymers. The combination of the obviously broad solvent/surface interface and the possibility of increased side reactions complicated the application of this reaction to the surface selective oxidation of hydrocarbon polymers.

Trifluoroperacetic Acid Oxidation of PE and PP

The reaction of TFPAA with linear alkanes produces a mixture of secondary alcohols and their trifluoroacetates (TFA).[34-36] For reactions with secondary carbon substrates in solution, no further oxidation to ketones was observed. Reaction of TFPAA with PE and PP gave surfaces which showed the incorporation of oxygen and fluorine by XPS as shown in Scheme 6.4 . Table 6.2 shows the XPS atomic compositions for a variety of reaction conditions. The 75° takeoff angle spectra consistently showed a slightly lower percentage of fluorine by 1-2%, relative to the 15° takeoff angle spectra. Because the 15° and 75° takeoff angle spectra represent the outermost 10Å and 40Å of the surface, respectively, we assumed that harsher conditions (higher temperatures, longer times) would lead to an increase in the density of functional groups. The XPS data shown in Table 6.2 indicates that at longer reaction times, higher reagent concentrations and reflux conditions do not affect the slight difference between grazing and normal angle XPS atomic compositions. The small difference may only have been indicative of the fact that

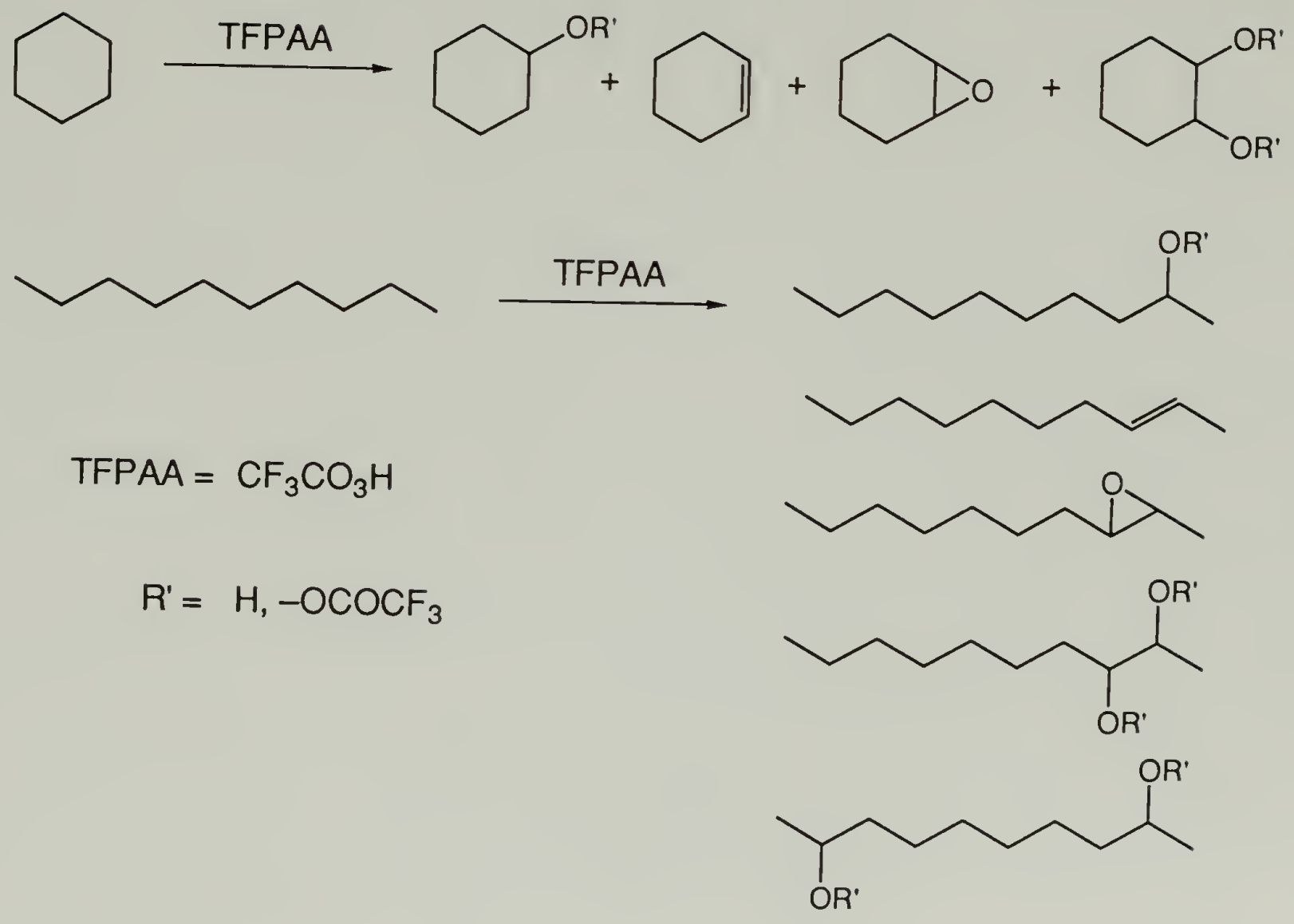


R = H (Polyethylene)

R = CH_3 (Polypropylene)

~~4~~ 108/44

Scheme 6.4. TFPAA Oxidation of Hydrocarbon Substrates. (Continued Next Page)



Scheme 6.4. Cont.

Table 6.2. XPS Atomic Composition Data for TFPAA Oxidation of PE and PP (Continued Next Page)

ESCA#	Sample#	XT	Reaction Conditions	Polymer	Angle	S/M	C=100	O(100)	F(100)	TFA(100)	OH(100)	Total#(100)
541		y	PP - virgin control	PP	15	M	100	2	—	—	2	2
526			PE, newly pressed, bottle	HDPE	15	M	100	3	—	—	3	3
528			PE, xylene ppt	HDPE	15	M	100	0	—	—	0	0
372	43A		TFPAA	LDPE	15	S	100	3	1	0	2	3
373	43A		TFPAA	LDPE	75	S						
537	49A		TFPAA x 1, 24 h	LDPE	15	M	100	7	5	2	4	6
539	49A		TFPAA x 1, 24 h	LDPE	75	S	100	6	3	1	4	5
834	72A		TFPAA x1, 20hr, sonicated	PP	15	M	100	4	1	0	4	4
835	72A		TFPAA x1, 20hr, sonicated	PP	75	S	100	2	0	0	2	2
841	72B		TFPAA x1, 20h, reflux	PP	15	M	100	12	16	6	1	7
843	72B		TFPAA x1, 20h, reflux	PP	75	M	100	9	16	6	0	4
940	72B		TFPAA x1, 20h, reflux	LDPE	15	M	100	9	5	2	6	7
942	72B		TFPAA x1, 20h, reflux	LDPE	75	M	100	9	4	1	6	7
1110	72B		TFPAA x1, 20 h, migration check	PP	15	M	100	10	13	5	2	7
1112	72B		TFPAA x1, 20 h, migration check	PP	75	M	100	8	11	4	0	4
827	72C	Y	TFA - Control sonicated 20h	PP	15	M	100	3	—	—	3	3
838	72D	Y	TFPAA x1, 20h, rflx-CTRL	PP	15	M	100	4	—	—	4	4
839	72D	Y	TFPAA x1, 20h, rflx-CTRL	PP	75	S	100	2	—	—	2	2
1053	76A	Y	TFA control, 20h reflux, bubbler	PP	15	M	100	2	0	0	2	2
1055	76A	Y	TFA control, 20h reflux, bubbler	PP	75	S	100	2	—	—	2	2

Table 6.2, Cont.

ESCA#	Sample#	XT	Reaction Conditions	Polymer	Angle	S/M	C=100	O(100)	F(100)	TFA(100)	OH(100)	Total#(100)
1057	76A	Y	TFA control, 20h reflux, bubbler	HDPE	15	M	100	1	0	0	1	1
1059	76A	Y	TFA control, 20h reflux, bubbler	HDPE	75	S	100	1	0	0	1	1
1062	76B		TFPAA x1, 20h reflux, Bubbler	PP	15	M	100	8	8	3	3	6
1077	76B		TFPAA x1, 20h reflux, Bubbler	HDPE	15	M	100	8	6	2	4	6
1079	76B		TFPAA x1, 20h reflux, Bubbler	HDPE	75	M	100	6	4	2	3	5
1041	78A		TFPAA x1, 12h reflux, air	HDPE	15	M	100	7	6	2	3	5
1043	78A		TFPAA x1, 12h reflux, air	HDPE	75	S	100	6	4	1	3	5
1045	78A		TFPAA x1, 12h reflux, air	PP	15	M	100	4	2	1	3	3
1047	78A		TFPAA x1, 12h reflux, air	PP	75	S	100	4	2	1	3	3
1037	78B		TFPAA x2, 12h reflux, air	HDPE	15	M	100	7	7	2	2	5
1039	78B		TFPAA x2, 12h reflux, air	HDPE	75	S	100	7	7	2	3	5
1048	78B		TFPAA x2, 12h reflux, air	PP	15	S	100	3	3	1	1	2
1049	78B		TFPAA x2, 12h reflux, air	PP	15	M	100	3	2	1	1	2
1051	78B		TFPAA x2, 12h reflux, air	PP	75	S	100	3	2	1	2	2
1094	80A		TFPAA x1, 8.5h reflux, N2	HDPE	15	M	100	8	10	4	2	5
1096	80A		TFPAA x1, 8.5h reflux, N2	HDPE	75	S	100	6	6	2	2	4
1102	80A		TFPAA x1, 8.5h reflux, N2	PP	15	M	100	5	3	1	3	4
1104	80A		TFPAA x1, 8.5h reflux, N2	PP	75	S	100	3	2	1	2	3
1098	80B		TFPAA x2, 8.5h reflux, N2	HDPE	15	M	100	9	8	3	3	6
1100	80B		TFPAA x2, 8.5h reflux, N2	HDPE	75	S	100	6	6	2	3	5
1106	80B		TFPAA x2, 8.5h reflux, N2	PP	15	M	100	4	2	1	3	4
1108	80B		TFPAA x2, 8.5h reflux, N2	PP	75	S	100	3	1	0	3	3

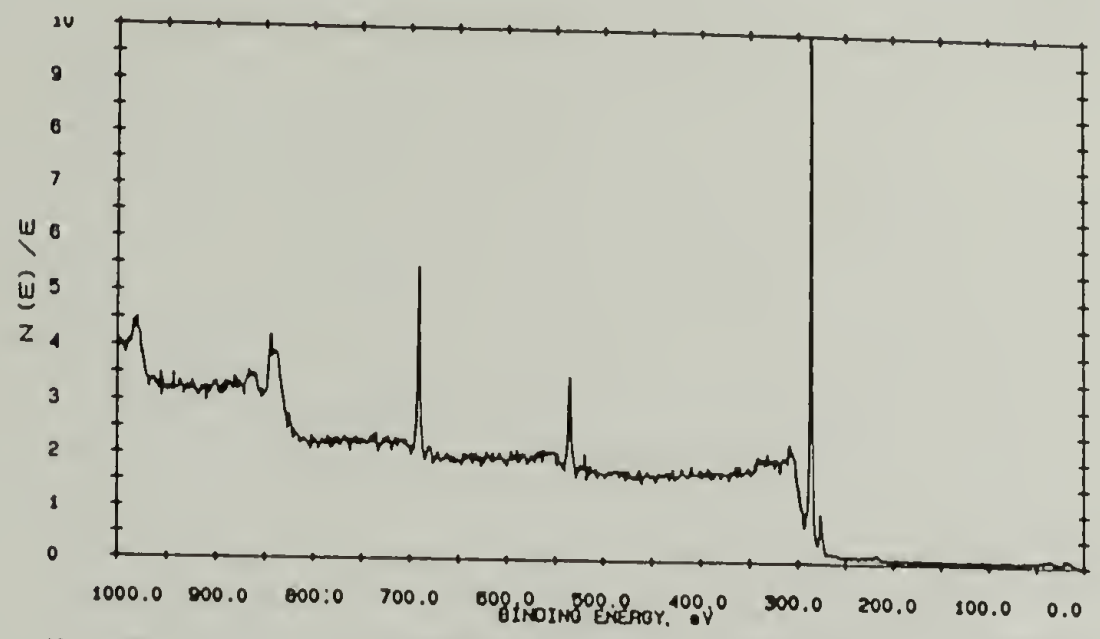
the trifluoromethyl group positions itself on the outermost surface in order to minimize surface energy, or correspondingly, that the polar carbonyl and hydroxyl groups bury themselves within the bulk of the film, forcing the trifluoromethyl group to face outwards.[37]

We elected to study the reaction of TFPAA with PE over time after preliminary labeling studies indicated that hydroxyl groups on the PE-[O]-TFA surface could be labeled. Figure 6.3 shows XPS spectra of a PE surface (a) after reaction with TFPAA, (b) after base hydrolysis and (c) after labeling with HFBC. Clearly, the functional groups on this surface were capable of reacting with an acid chloride; hydroxyl groups were the most likely candidates. Reaction of PE and PP films with TFPAA at reflux (84°C) resulted in a surface with an average "repeat unit" of 100/3/4 (C/TFA/[O]) The [O] in this expression refers to oxygen present by XPS which cannot be assigned to the acetate moiety. If we assume that all of this oxygen is present in the form of hydroxyl groups, then less than 10% of the carbon atoms are attached to trifluoroacetate (TFA) or hydroxyl OH groups.

Relative to other surface modifications studied in our group, this surface repeat unit does not represent an extensively modified surface, but we chose to study this reaction in more detail because the combination of hydroxyl and trifluoroacetate groups indicated on the surface represented and interesting "protected" surface. The acetate groups can be easily removed under basic hydrolysis conditions to reveal a hydroxyl surface.

We chose to conduct our time dependent study at reflux conditions, such that the amount of functionalization could be followed at shorter reaction times using XPS. We selected PE over PP because tertiary carbons were reported to result in the formation of ketones and rearrangement products and the distribution of products would be simpler for PE.[34-35] In addition, clean HDPE (<0.5% [O]) could be made relatively easily and

Trifluoroperacetic Acid Oxidation of Polyethylene

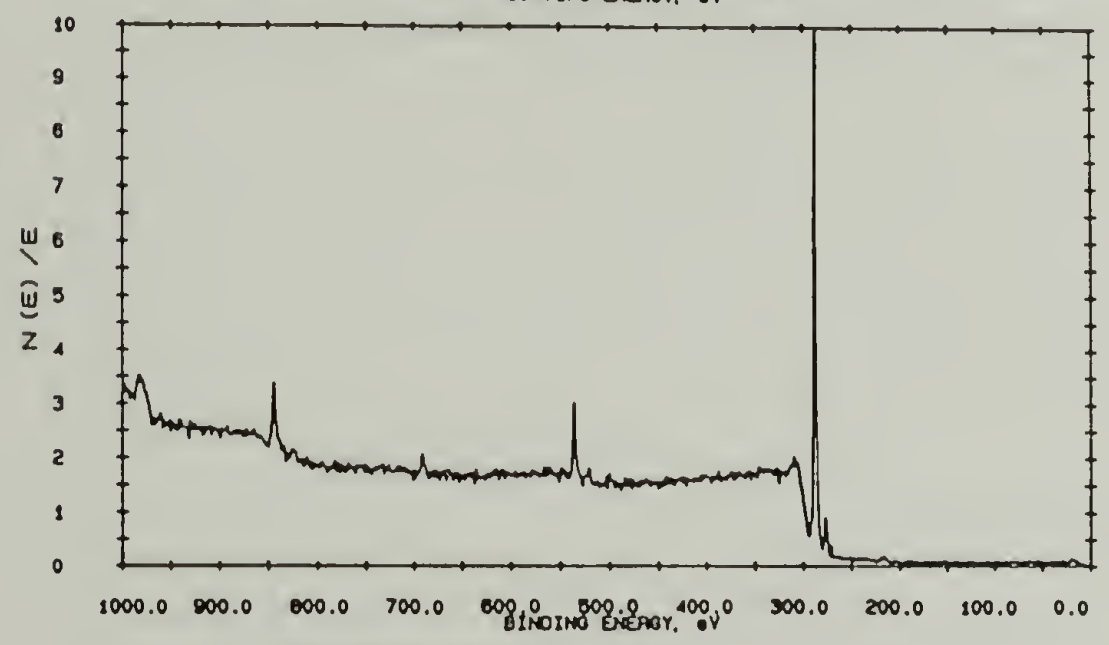


XPS Survey Spectrum (15°)

Atomic Composition

Carbon	85.44
Oxygen	7.44
Fluorine	7.12

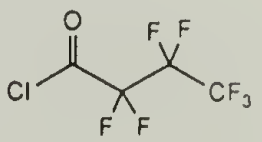
OH⁻

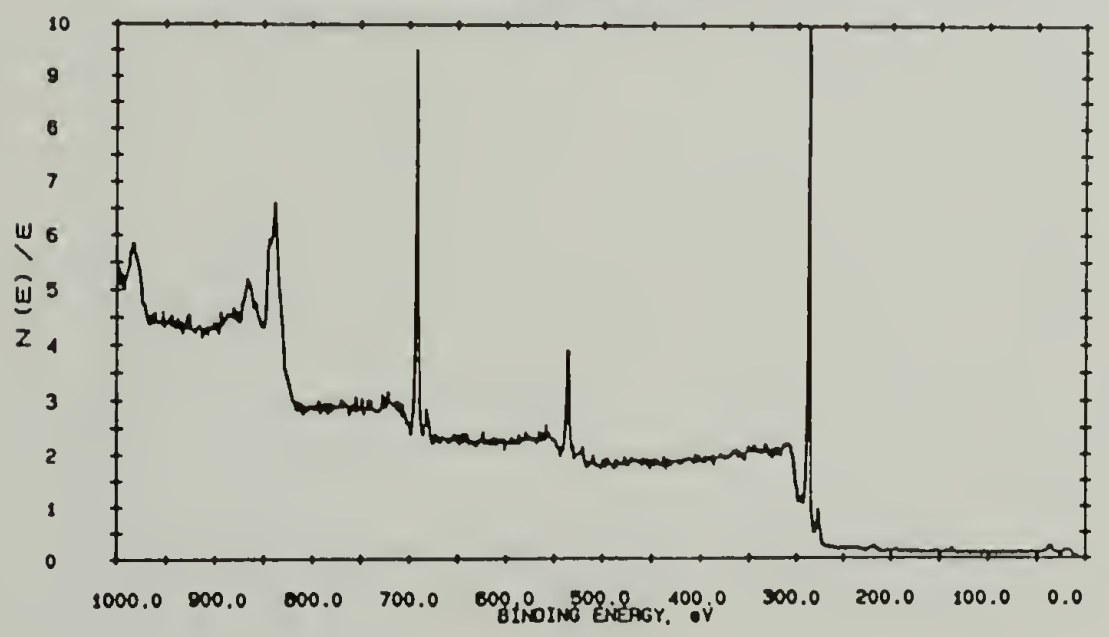


XPS Survey Spectrum (15°)

Atomic Composition

Carbon	94.06
Oxygen	5.21
Fluorine	0.61





XPS Survey Spectrum (15°)

Atomic Composition

Carbon	83.92
Oxygen	5.45
Fluorine	10.63

Figure 6.3. XPS Spectra of the TFPAA Oxidation and Labeling of a PE Surface. (a) After reaction with TFPAA, (b) After base hydrolysis and (c) After labeling with HFBC.

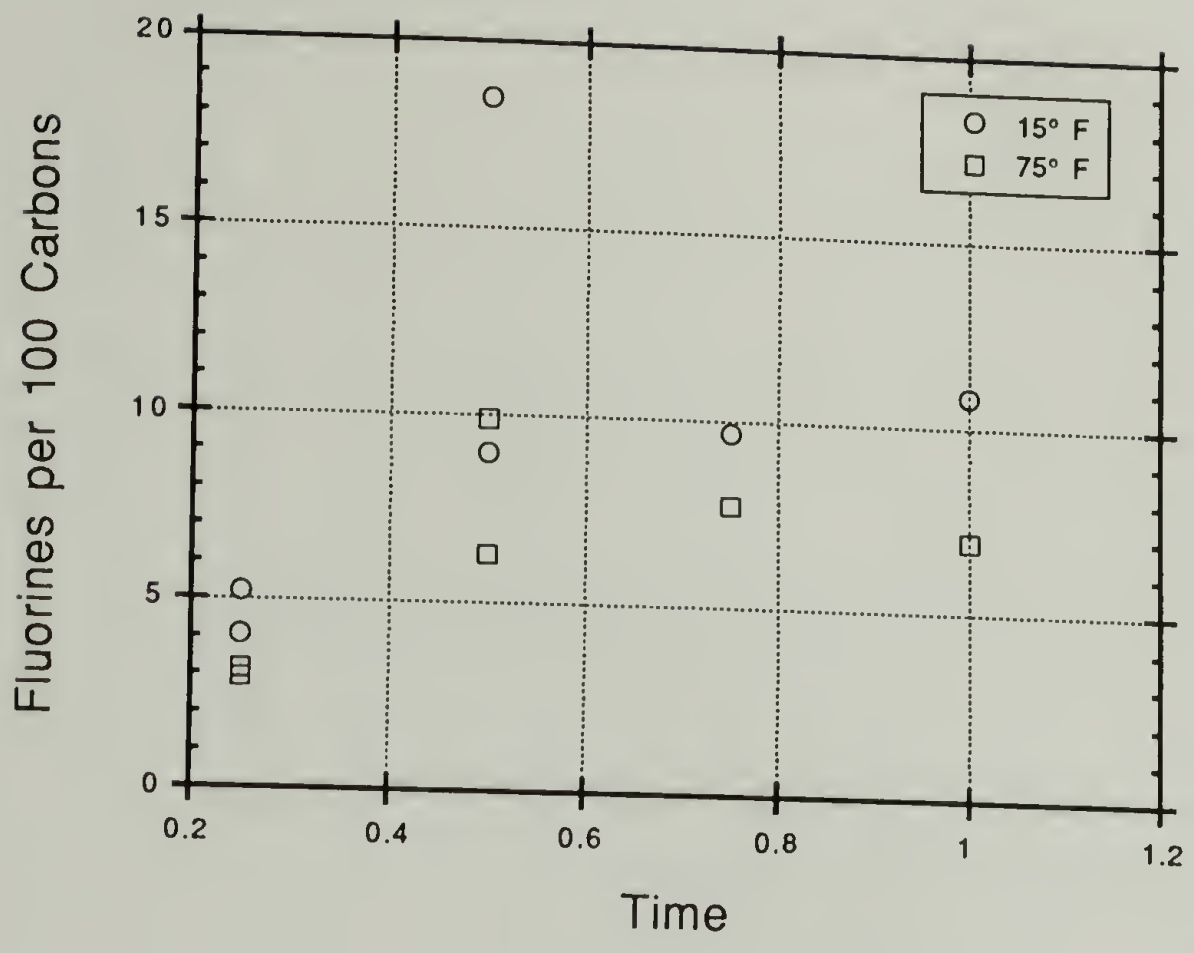
reproducibly. Ultimately, we wanted to use the combination of time, temperature and solvent to control the depth of reaction, the sharpness of the interface and the relative number of hydroxyl and TFA groups incorporated using this reaction.

Rate of TFPAA Oxidation of PE

A series of reactions were run over a period of 24 h under reflux conditions to explore the reaction of TFPAA over time. Samples were evaluated by XPS, ATR-IR, UV-VIS, contact angle and gravimetric analysis and the results are shown in Figures 6.4-6.9. Initially, this reaction was monitored at the 1, 3, 6, 12 and 24 h points. As shown in the gravimetric results in Figure 6.9 however, the three samples for the 1 h reaction had already gained 152, 153 and 183 μg, respectively. In order to follow the initial stages of the reaction more carefully, additional films were reacted for 0.25, 0.50 and 0.75 hours.

XPS of PE-[O]-TFA Surfaces Reacted over 24 h

XPS atomic composition results are shown in Figures 6.4-6.5, as the percentage of fluorine and oxygen on the surface, respectively. Each was normalized to 100 carbon atoms so that we could compare surfaces with respect to a common repeat unit. We examined both 15° and 75° takeoff angles and the data for both the first hour and the 24 h period are plotted. As discussed previously, the 1-2% difference between the 15° and 75° takeoff angle spectra was not large enough to indicate a chemical composition gradient within the outer 40Å of the film.[38] These numbers are heavily weighted toward the outer 10Å, because the information available from XPS falls off exponentially as one proceeds toward the bulk of the film. However, we can see a gradual increase in the incorporation of both oxygen and fluorine onto the surfaces over the first 12 h of the reaction before it levels off.



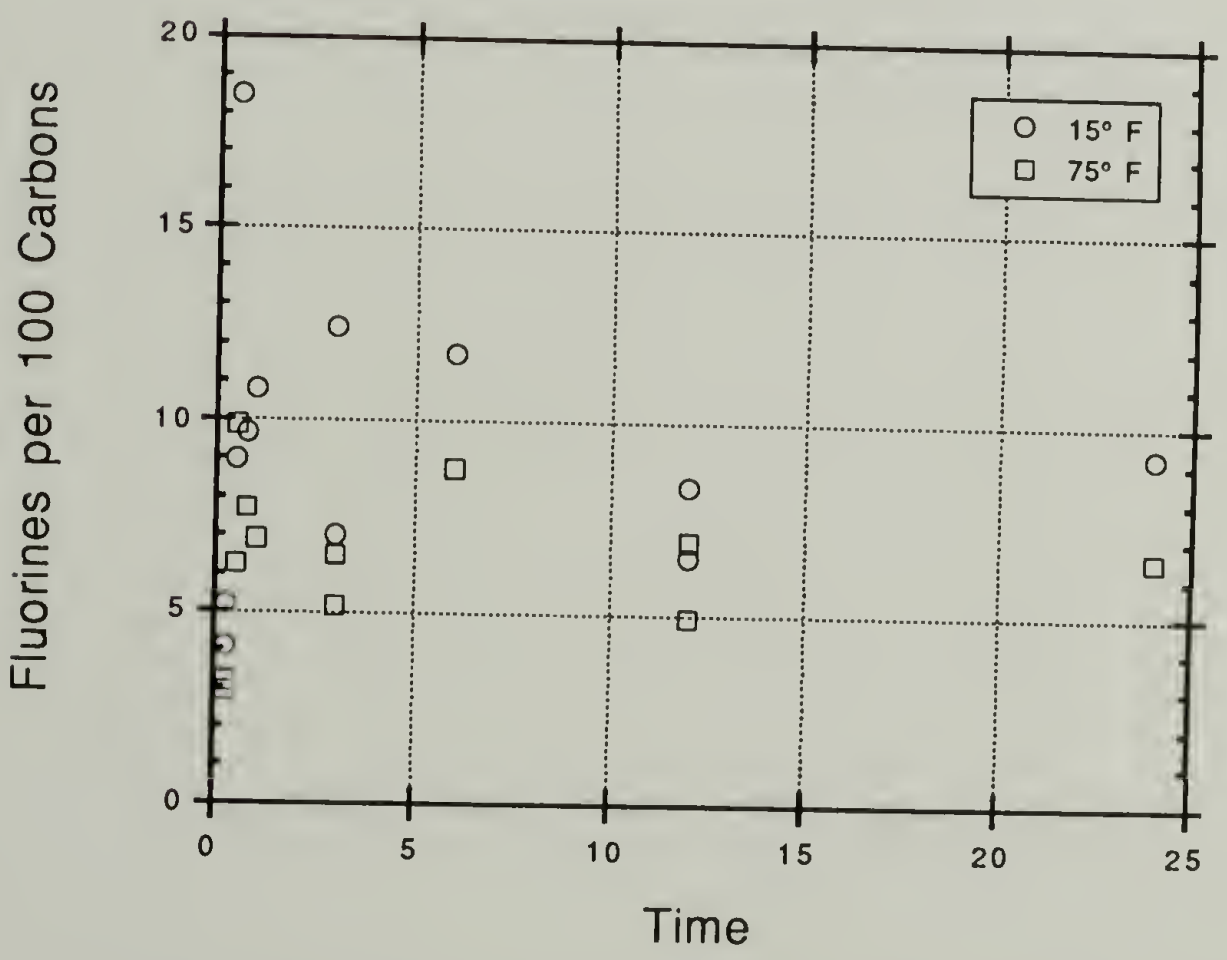


Figure 6.4. XPS Atomic Composition Data: Number of Fluorine Atoms per 100 Carbon Atom Repeat Unit over Time. TFPAA Oxidation of HDPE for (a) 1 h (b) 24 h

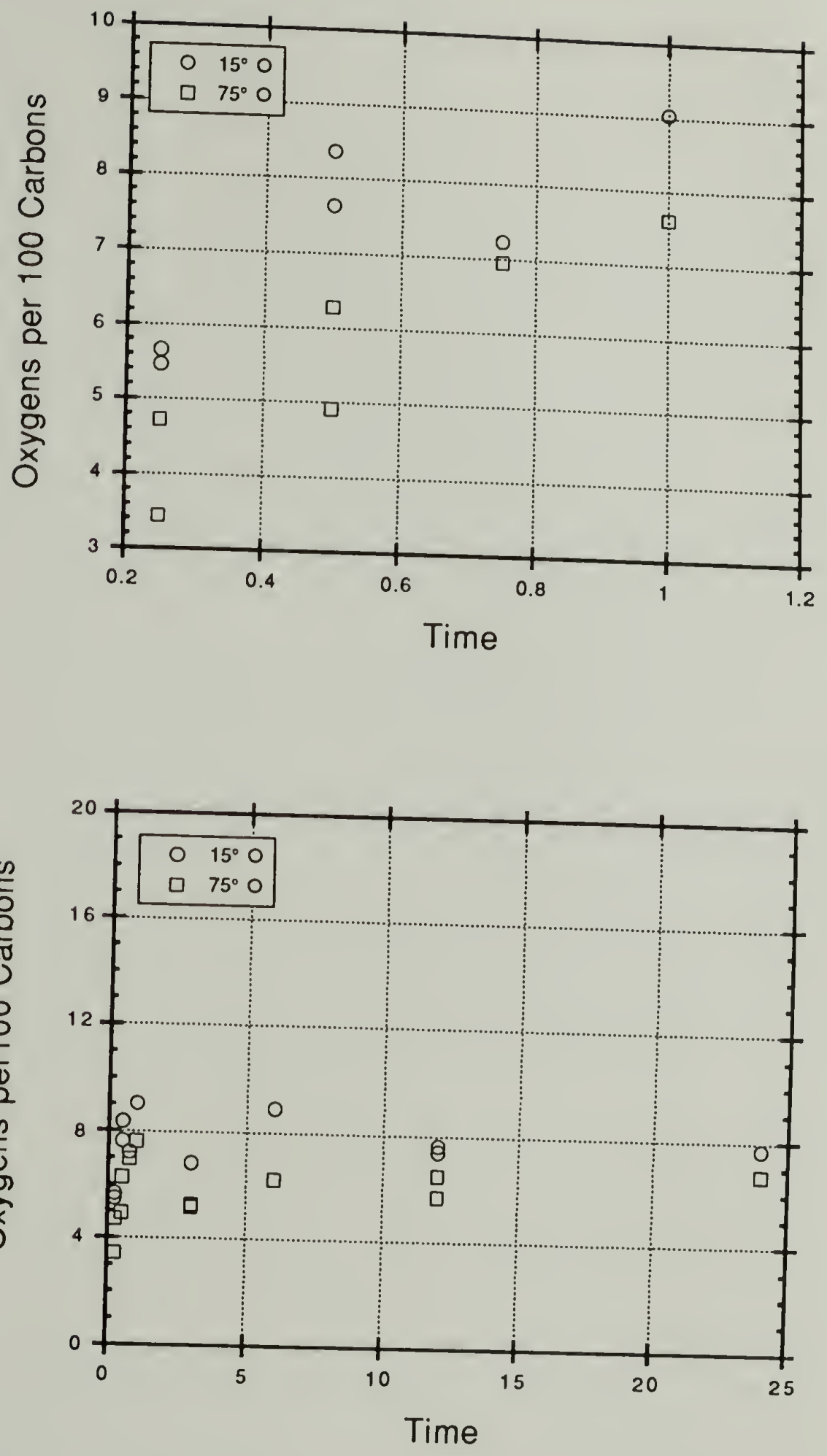


Figure 6.5. XPS Atomic Composition Data: Number of Oxygen Atoms per 100 Carbon Atom Repeat Unit over Time. TFPAA Oxidation of HDPE for (a) 1 h (b) 24 h

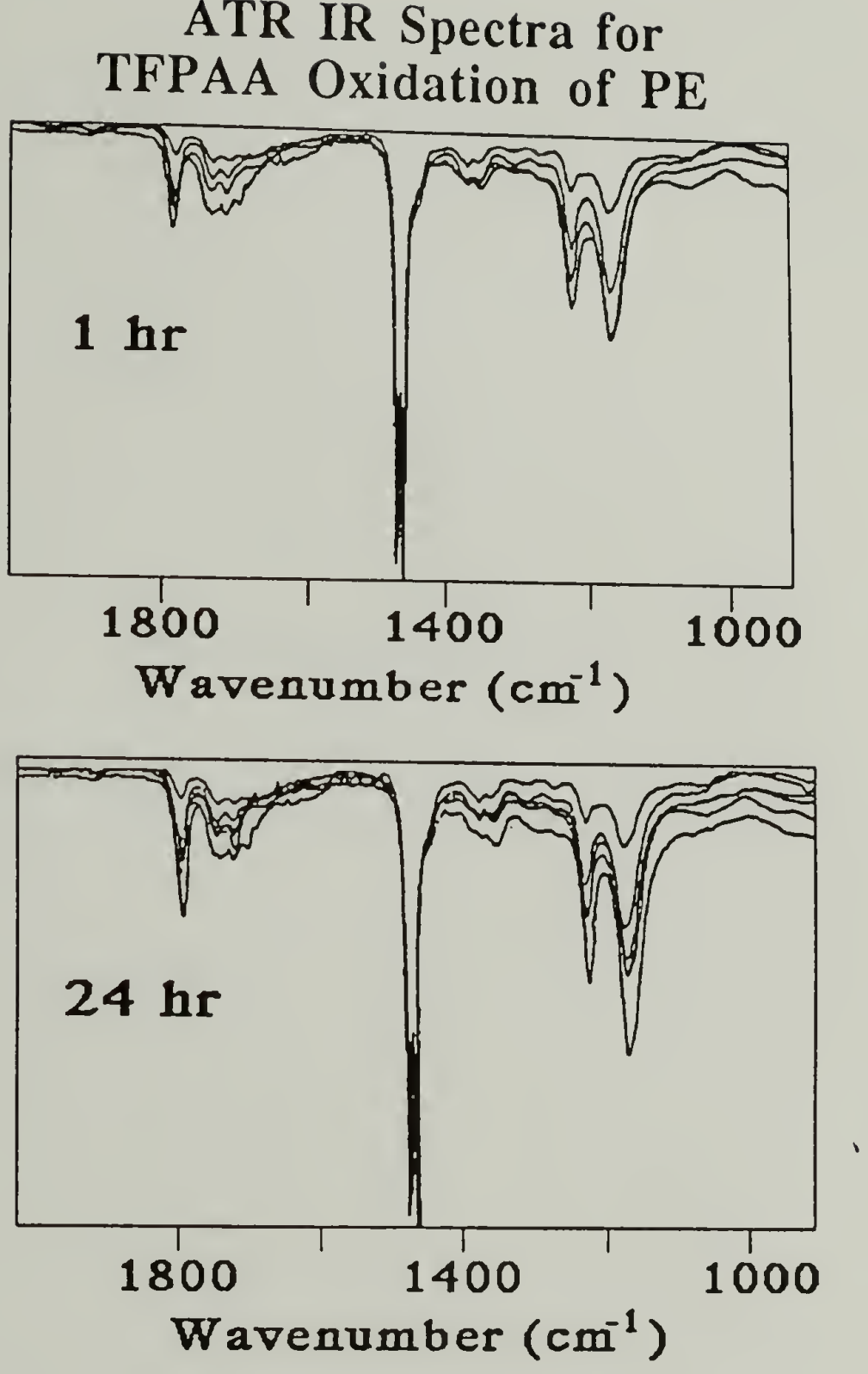
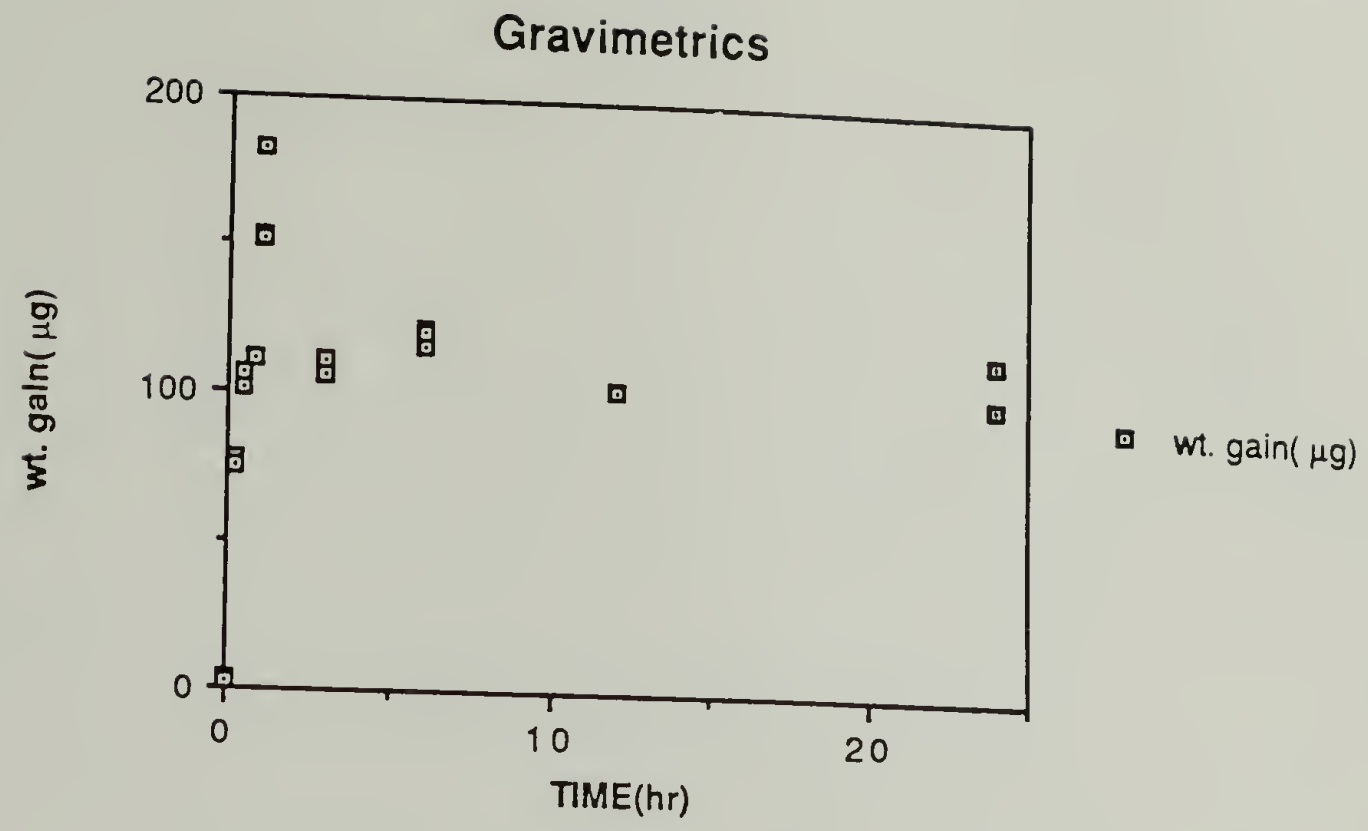


Figure 6.6. ATR-IR Spectra: Overlayed to Show the Increase in TFA Concentration over Time. TFPAA Oxidation of HDPE for (a) 1 h (b) 24 h;



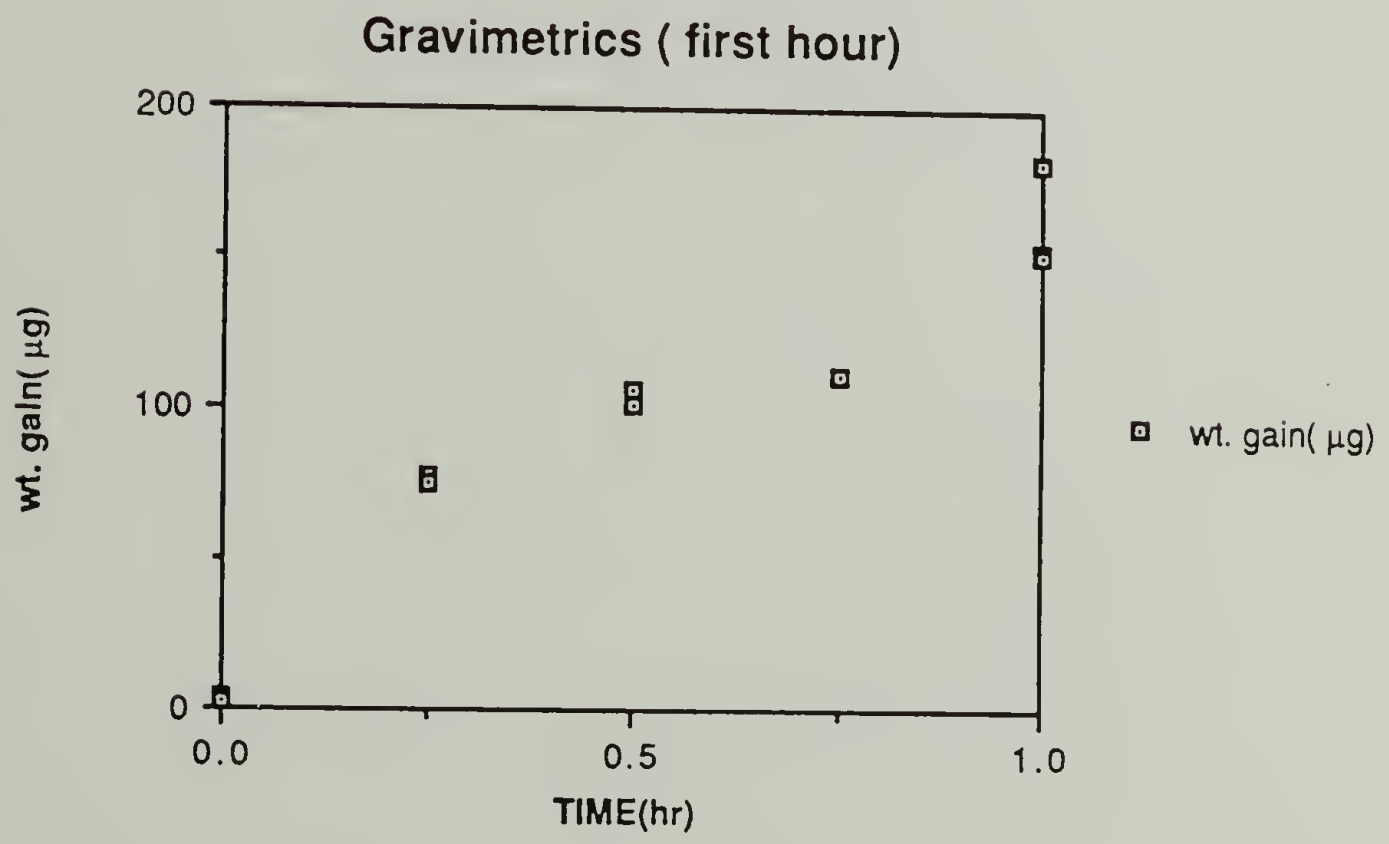
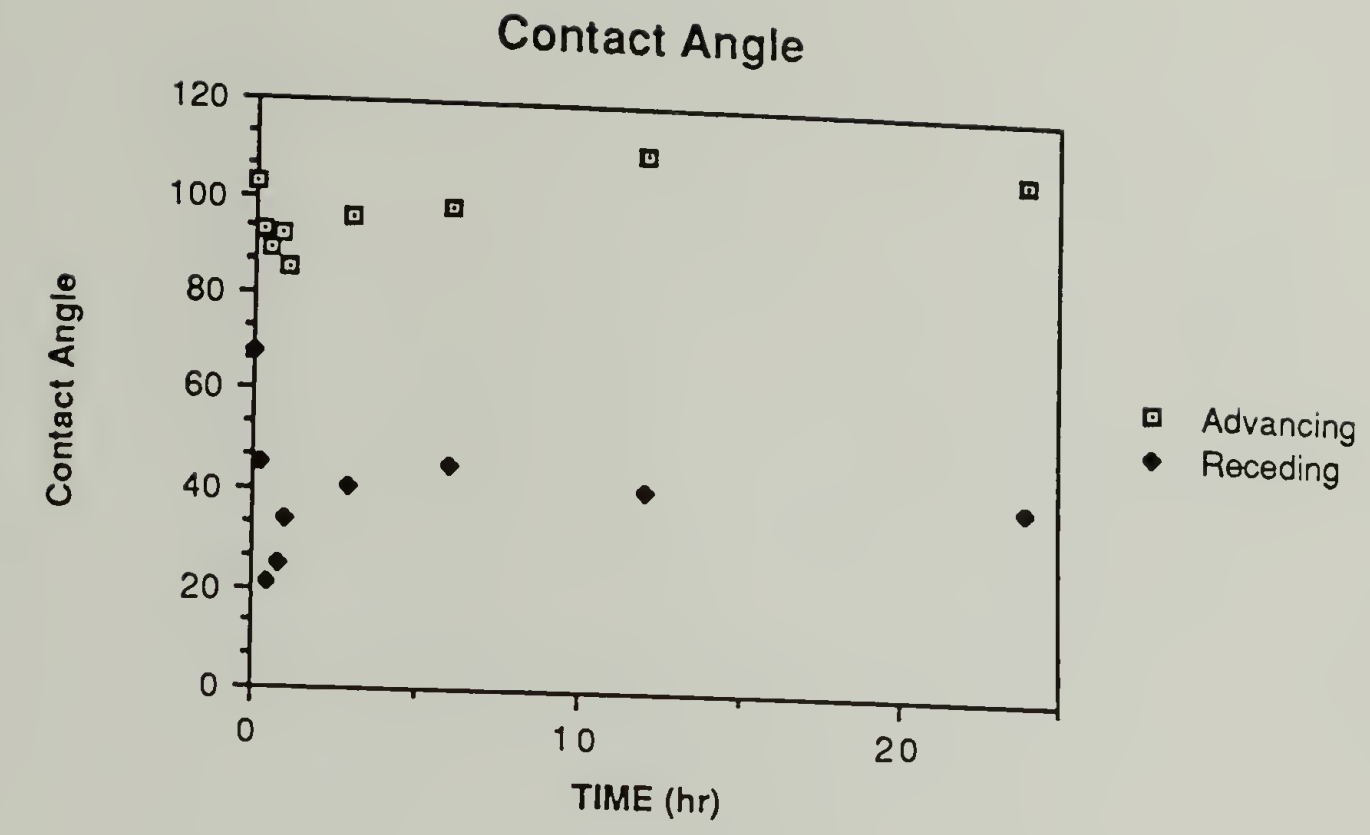


Figure 6.7. Gravimetric Data to Show the Weight Gain over Time. TFPAA Oxidation of HDPE for (a) 1 h (b) 24 h



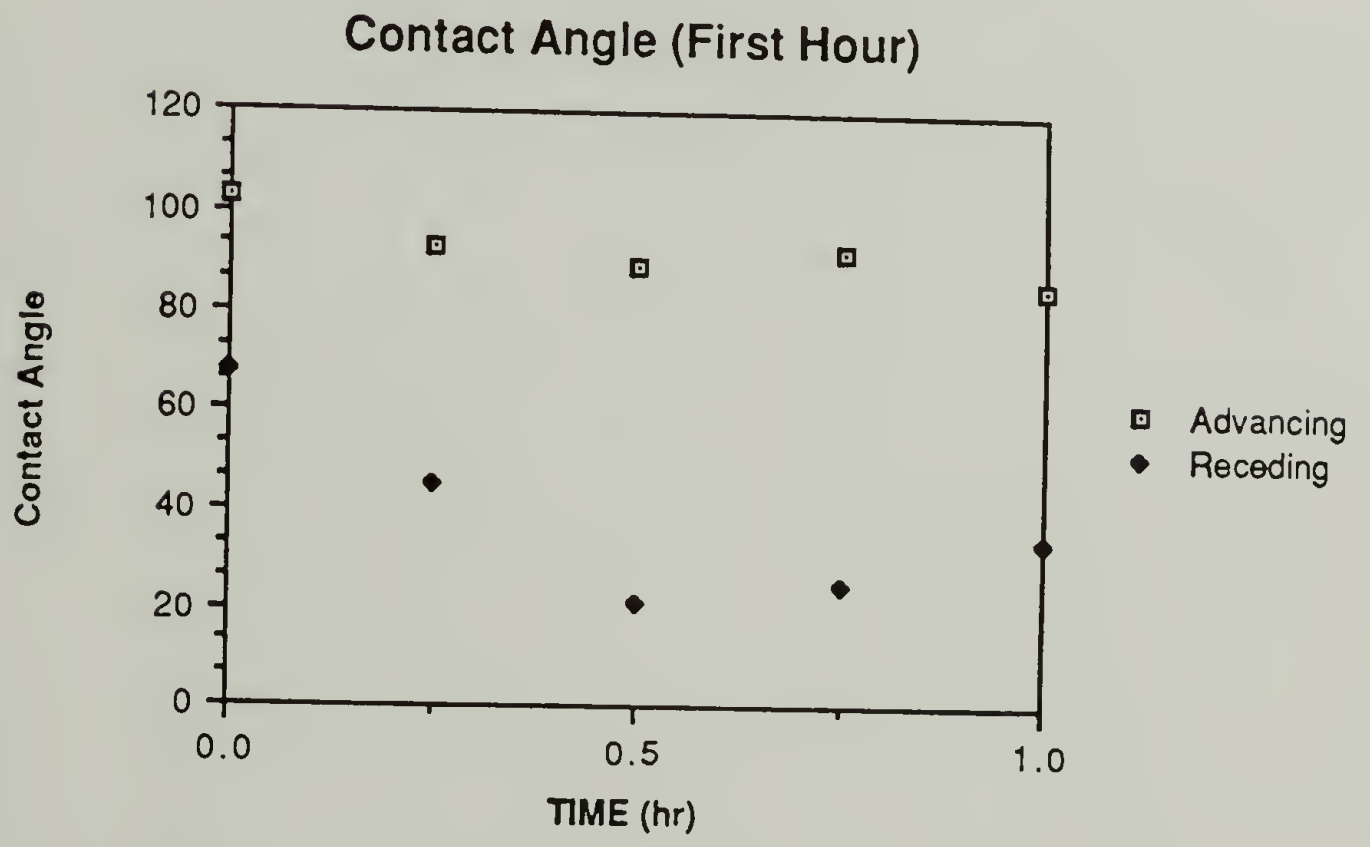
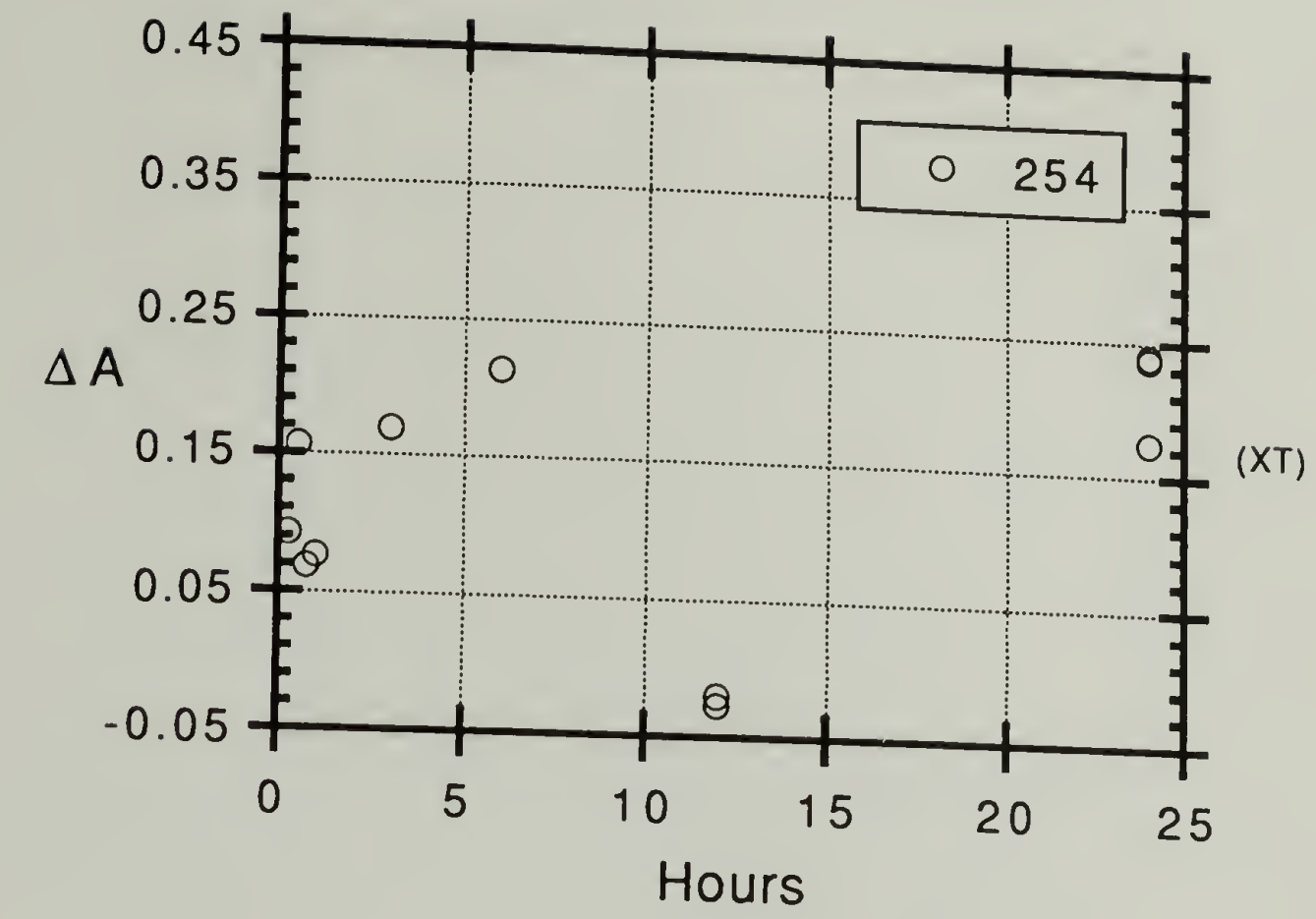


Figure 6.8. Contact Angle Data to Show Changes in Surface Free Energy over Time. TFPAA Oxidation of HDPE for (a) 1 h (b) 24 h



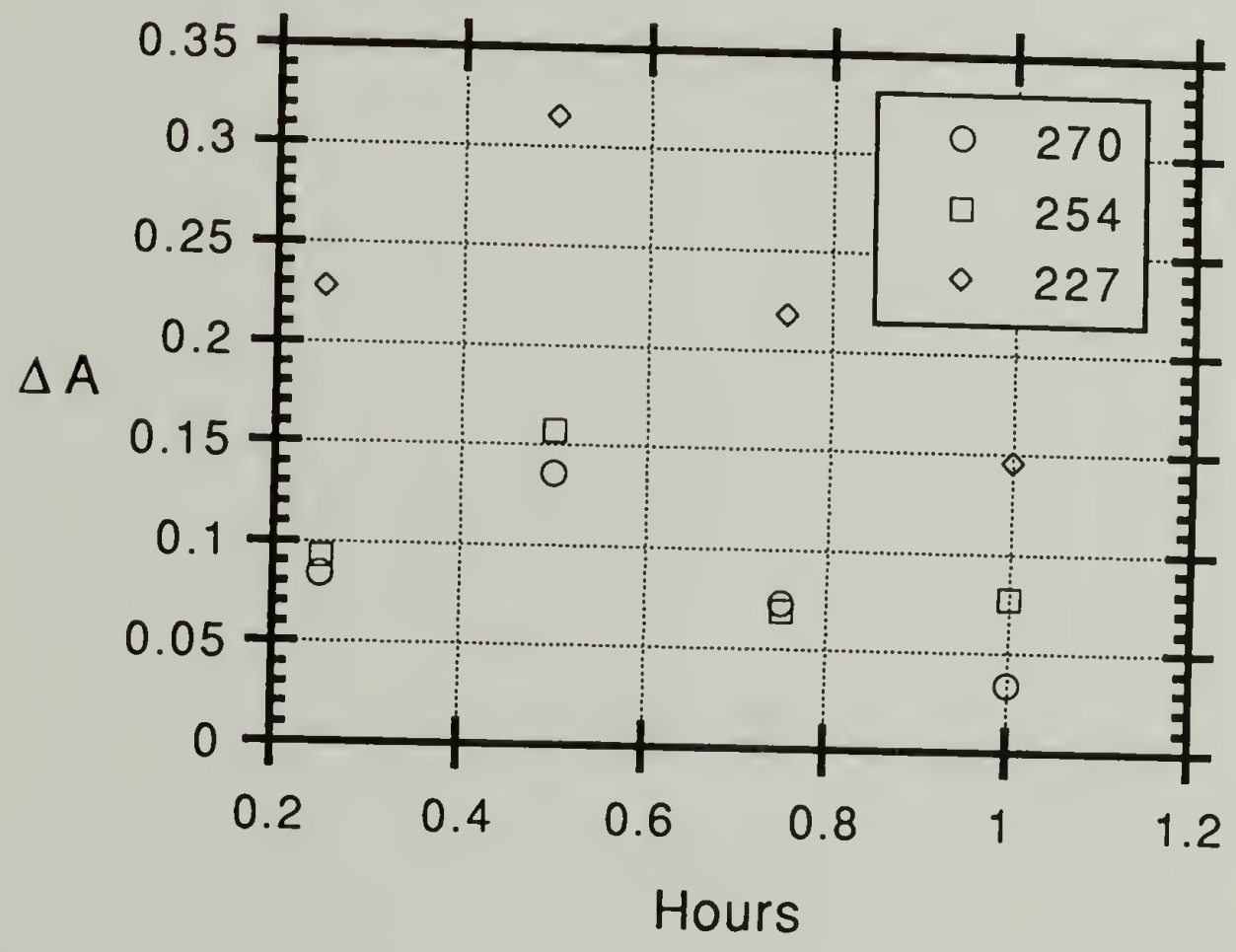


Figure 6.9. UV-VIS Data to Show the Absorbance (254 nm) over Time. TFPAA Oxidation of HDPE for (a) 1 h (b) 24 h

In calculating the 100 carbon repeat unit, we assumed that all of the fluorine on the surface was due to TFA groups. This was divided by three to give the number of TFA groups, and the number of oxygen and carbon atoms due those TFA groups was subtracted from the initial percentages of oxygen and carbon. This is referred to as the adjusted composition, and it was used to determine the number of TFA and other types of oxygen functionalities present per 100 carbon unit.

ATR-IR of PE-[O]-TFA Surfaces Reacted over 24 h

ATR-IR spectra for the 24 h series and for unreacted PE are shown in Figure 6.6. The ATR-IR of virgin PE is relatively simple. The C-H stretching bands are sharply defined at 2918 and 2849 cm^{-1}, as are the C-H bending modes at 1473 and 1462 cm^{-1}. Reaction with TFPAA led to sharp absorbances at 1784 (C=O stretching), 1223 and 1169 (C-F bending) typical of alkyl trifluoromethyl esters. The broad bands at 1650-1700 cm^{-1} could be due to weak olefin carbon-carbon bands. We also saw carbonyl stretching bands at 1732 and 1713 which were attributed to ester and ketone functionalities for reasons which will be discussed in the surface derivatization section. These spectra cannot be considered to be absolutely quantitative because of the variations in intensity due to differences in the pressure used to clamp the samples to the crystal. However, the absorbances at 1784 as well as at 1223 and 1169 clearly increased relative to the C-H bending bands at 1473 and 1462 over the course of the 24 h reaction, indicating that more trifluoroacetate groups were incorporated over time within the ATR sampling depth. No clear evidence of hydroxyl groups was observed in the O-H stretch region, but in our experience these have been absent in the ATR-IR spectra of other hydroxylated surfaces as a result of the relatively low extinction coefficient of O-H stretching bands, even when the presence of hydroxyl groups is clearly indicated by other analyses.

Gravimetric Results for PE-[O]-TFA Surfaces Reacted over 24 h

We can compare the weight gained by the different samples because each sample was cut to the same dimensions and, as a result, should have the same amount of reactive surface area. Weight changes on the order of 100 μg are quite large, relative to other reactions that we have followed by gravimetric analysis; this indicates that the depth of reaction is quite deep for this reaction under these conditions As shown in Figure 6.7, the films gain weight quickly over time, leveling off after one hour at the 100-120 μg level. The relatively high values for the one hour sample are difficult to explain. If we discount the 183 μg value as anomalous, the values of 152 μg and 153 μg are still 25% higher than the next highest values of 122 μg at 6 hours. A significantly higher density of functional groups or greater proportion of TFA groups as opposed to alcohols at the one hour point would cause the molecular weight of the modified layer to be higher than at other times during the reaction, accounting for the discrepancy in weight gain, but XPS data does not support either of these possibilities, as shown in Figures 6.4and 6.5. Two conclusions follow: First, the weight gain could be due to changes not reflected in our other data. Second, the three gravimetric film samples for the one hour reaction must have a greater surface area for reaction. They may have been cut from a strip of PE which was wider in one dimension than for the other samples. Alternatively, an artifact of the pressing procedure could have created a rougher surface and consequently greater surface area. As a final note, the fact that the gravimetric samples all gained weight over time does not necessarily mean that no bond breaking or chain scission has occurred. The polar functionalities on the modified chains should lend them a certain solubility in trifluoroacetic acid, and if any chain scission is occurring, we would expect these surfaces to dissolve into the trifluoroacetic acid at the same time that the heavier modified layer is forming. The fact that the overall weight gain is still positive after 24 h indicates that the amount of PE dissolving is minimal.

Contact Angle Results for PPE-[O]-TFA Surfaces Reacted over 24 h

Contact angle measurements, when applied as a qualitative tool, help us to compare the relative surface energies of modified surfaces. Plots of the advancing and receding contact angles for the 24 h period and over the first hour are shown in Figure 6.8. The decrease in both the advancing and receding contact angles even after 0.25 hours indicates a higher energy surface, and the hysteresis between the advancing and receding angles can be attributed to inhomogeneity in the chemical composition. The receding angle reached a minimum of 20° at 0.5 h, representing the greatest increase in surface free energy over the course of the reaction. Chemically, we could assign this to a peak in the population of hydroxyl groups on the surface before they react with the solvent to form TFA groups. The low initial receding contact angles could also be representative of a small number of low surface energy groups incorporated onto the surface. Incorporation of additional trifluoromethyl group leads to higher advancing and receding contact angles. The primary alcohols initially formed may not be immediately vulnerable to esterification until the chains have been modified extensively enough to be swollen by trifluoroacetic acid. The receding angle minimum may represent the time required to achieve sufficient functionalization. After a gradual increase, the contact angles level off after several hours at 92/47, suggesting that after extended periods of reaction, most of the hydroxyl groups are present as their trifluoroacetates.

UV-VIS Results for PE-[O]-TFA Surfaces Reacted over 24 h

Data was taken for the changes in absorbance at 227, 240, 250, 254, 260, 270 and 300 nm,. The results at 254 nm for the 24 h reaction and 227, 240 and 254 nm for reaction times up to 1 h are plotted in Figure 6.9. All of the films turned a light brown color over the course of the reaction, but much of the sample color disappeared after the films were rinsed with methanol. Even the 0.25 h samples were slightly discolored. The

maximum change between the reacted and unreacted samples (0.25 absorbance units) was not large. This was not surprising, because we would not expect a large change for a reaction which reportedly produced non-conjugated alcohols and carbonyls.

Of all the possible products, the TFA esters are the most likely cause of the increase in absorbance of the products. As the reaction proceeds through the depth of the film, the number of hydroxyl and their trifluoroacetate groups increases, but due to the inhibiting effects of previously formed hydroxyl and TFA groups, the double bonds formed by elimination of the TFA groups are not likely to be in close proximity to each other. As a result, they should not be conjugated and should not contribute significantly to the absorbance spectrum of the product films.

Trifluoroacetic acid alone does not absorb strongly in this region, and we would not expect non-conjugated TFA esters to have significantly different absorbance characteristics. However, the increase in the absorbance (0.15 units) of the control film which was refluxed in trifluoroacetic acid for 24 h indicates that the absorbance changes for all of these films may have been due to residual solvent (trifluoroacetic acid) trapped in the films. It makes sense that films which had been exposed to refluxing trifluoroacetic acid for shorter periods of time would show less evidence of residual solvent, but when the 12 and 24 h samples were remeasured, after drying for several more days the new values were identical to the original ones. These two samples may have already been sufficiently dry prior to the initial weighing, but the other samples were not remeasured to test this theory out.

Realistically, the absorbances change that we are concerned with here is quite small. They could be accounted for by slightly different placement of the films in the sample holder during the measurements. The anomalous data points for the 12 h sample can be accounted for if it was thicker at one end than the other and had been turned over

180° for the post reaction measurements. However, we can say that the TFPAA oxidation of PE does not produce large changes in the UV-VIS region of the spectrum; no extensive conjugation was indicated by the small absorbance increases.

Depth of Reaction Calculations for PE-[O]-TFA Surfaces

Using the number of TFA and [O] groups determined using the adjusted compositions discussed in the XPS section, we obtained a repeat unit of functional groups per 100 carbon atoms. To simplify the calculation of the molecular weight of the repeat unit, we assumed that any oxygen present which was not due to TFA groups was present as an OH group. If in fact the [O] is actually due to ketone or ester oxygen, the weight of the repeat unit does not change dramatically. This repeat unit was used to determine the depth of reaction, as calculated for the 0.25 h sample and shown in Scheme 6.5. Depths of reaction determined using this method are shown below in Table 6.3. These figures indicate that after only 15 min, up to 1 μm of material has been reacted.

Table 6.3 Depth of Reaction as Calculated using Scheme 6.5.

Time (h)	XPS #	#TFA Groups	#OH Groups	#CH_2 Groups	Mass Gain (μg)	Depth of Reaction (m)
0.25	1619	1.80	2.06	96.14	0.076	1.18
0.50	1568	7.03	0.00	92.97	0.103	0.64
0.75	1575	3.45	0.82	95.73	0.110	1.10
1.00	1512	3.90	1.95	94.15	0.153	1.36
3.00	1472	4.52	0.00	95.48	0.109	0.91
6.00	1571	4.26	1.14	94.59	0.119	1.01
12.00	1418	2.28	3.42	94.30	0.102	1.25
24.00	1463	3.30	1.64	95.07	0.108	1.09
XT	1415	0.26	2.38	97.36	0.003	0.15

As an example: Suppose that the XPS atomic composition indicates 4 TFA groups and 1 OH group per 100 carbons i.e. the modified repeat unit.

MW of the modified repeat unit

=	PE*	= 95 CH_2	=	1330g
		= 4(CH-CO_2CF_3)	=	504
		= (CH-OH)	=	30
				1864
MW of Virgin PE	= PE	= 100 CH_2	=	1400

Moles of PE* present in modified layer =Mass Gain/(PE*-PE)

For a weight gain of 100 μg: 100 μg x (1 mole/464g) = 2.2×10^{-7} Moles PE*

2.2×10^{-7} Moles PE* x 1864 g/molePE* = 4.02×10^{-4}

Assuming a density of 1g/ml for the modified layer and an area of $2.25cm^2$(1.5cm x 1.5cm), then the volume modified is equal to:

$$4.02 \times 10^{-4} \times cm^3/1g = 2.25cm^2$$

and the height of the layer necessary to accomodate this volume of PE* is

$$4.02 \times 10^{-4} / 2.25 = 1.78 \times 10^{-4} \text{ cm} = 1.78 \mu.$$

Each side of the film can react, so the actual thickness of the modified layer is 50% of this number:

$$1.78 \mu./2 = o.89 \mu.$$

Scheme 6.5. Calculation of a Minimum Depth of Reaction for PE-[O]-TFA Surfaces.

These represent a value for the minimum depth of reaction, because we used the functional group population for the 15° XPS spectra, which would give the greatest density of functional groups and thus the highest molecular weight for the repeat unit. We know that the 15° XPS spectra represent the atomic composition of the outer 10Å of the film, and that the 75° spectrum counts electrons from up to 40Å. However, since the escape depth falls off exponentially, we know that these atomic compositions are heavily weighted toward the outer 10-20Å of the film. The calculations detailed above assume that the atomic composition is homogeneous throughout the reacted layer. As a result, our calculation for the depth of reaction would give the thinnest layer which could account for the given weight gain. In other words, we have determined a minimum depth of reaction.

Derivatization of PE-[O]-TFA Surfaces

In order to obtain more information concerning the functional groups present on these PE-[O]-TFA surfaces, we reacted several film samples for 15 min to provide a set of samples for derivatization. We chose this reaction time because at this point, the reacted layer should be deep enough to see changes in functional group populations via ATR-IR, while at the same time shallow enough that we would be able to completely modify the depth sampled by the ATR-IR. The derivatized samples were also analyzed using XPS and contact angle (see Figure 6.10). ATR-IR results for these same reactions are shown in Figure 6.11. ATR-IR provided the most lucid information for the derivatization reactions because it showed differences in the relative populations of functional groups. Base hydrolysis (0.5 *M* NaOH/ 60°C) should cleave any TFA groups present to form hydroxyl groups. The BH_3/THF reduction with a basic peroxide workup should reduce any ketones or double bonds present, and the reactions with HFBC should enable us to identify the hydroxyl groups present on each type of surface by labeling them. We chose HFBC as opposed to trifluoroacetic anhydride because it would be easier to detect using XPS; seven

fluorine atoms are incorporated with each labeling reaction compared to three for the anhydride. As shown in Figure 6.11, after the reaction of the original PE-[O]-TFA surface with BH_3, most of the 1713 peak originally present as well as the broader absorbances from 1650-1700 have disappeared. The carbonyl bands at 1784 and 1732 are also smaller, indicating that some hydrolysis of the esters present may have occurred during the basic peroxide workup. This is supported by the loss of fluorine from the XPS sampling depth.

The effects of the reduction are not as clear when a TFA sample which has already been hydrolyzed is then reduced with BH_3. As shown in Figure 6.11, the two ATR spectra of the hydrolyzed and the hydrolyzed then reduced films appear almost identical. The XPS shows that the amount of oxygen present on the surface is slightly lower (~1%) and that a small amount of fluorine has been added to the film. Small amounts of residual HFBC may have been absorbed by these films while they were being stored on a vacuum line where samples which had been exposed to HFBC were drying. Alternatively, the HFBC contaminant may have reacted with surface hydroxyl groups. Both situations would lead to the incorporation of small amounts of HFBC on films where none would be expected, i. e. on the control films for the various derivatization reactions. Base hydrolysis of an original PE-TFA film gave the expected result of substantial decrease in the amount of fluorine indicated by XPS as well as a decrease in the size of the two ester peaks in the ATR-IR.

Labeling reactions of these hydrolyzed and reduced surfaces with HFBC showed a distinct increase in the amount of fluorine on the surfaces shown by XPS, and an increased ester peak at 1784 cm^{-1}. One would expect the biggest increases in fluorine to occur on the surface which had been hydrolyzed and then reduced, but the simply hydrolyzed surface showed a slightly larger incorporation of fluorine. Using the compositions adjusted for 100 carbon units, the PE-[O]-TFA-OH surface showed an uptake of 7 fluorines per 100

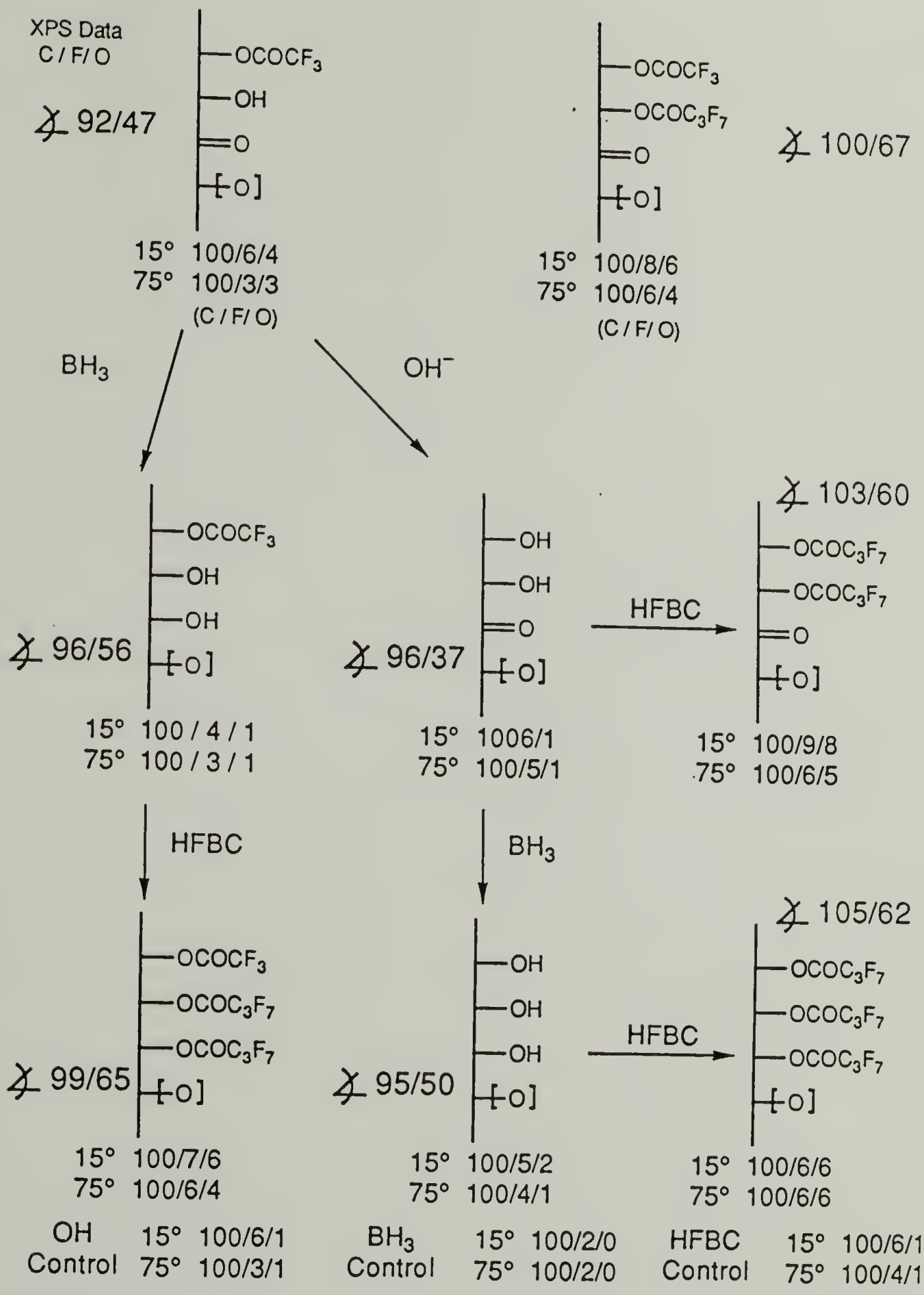


Figure 6.10. Contact Angles and XPS Atomic Compositions for Derivatized PE-[O]-TFA Surfaces.

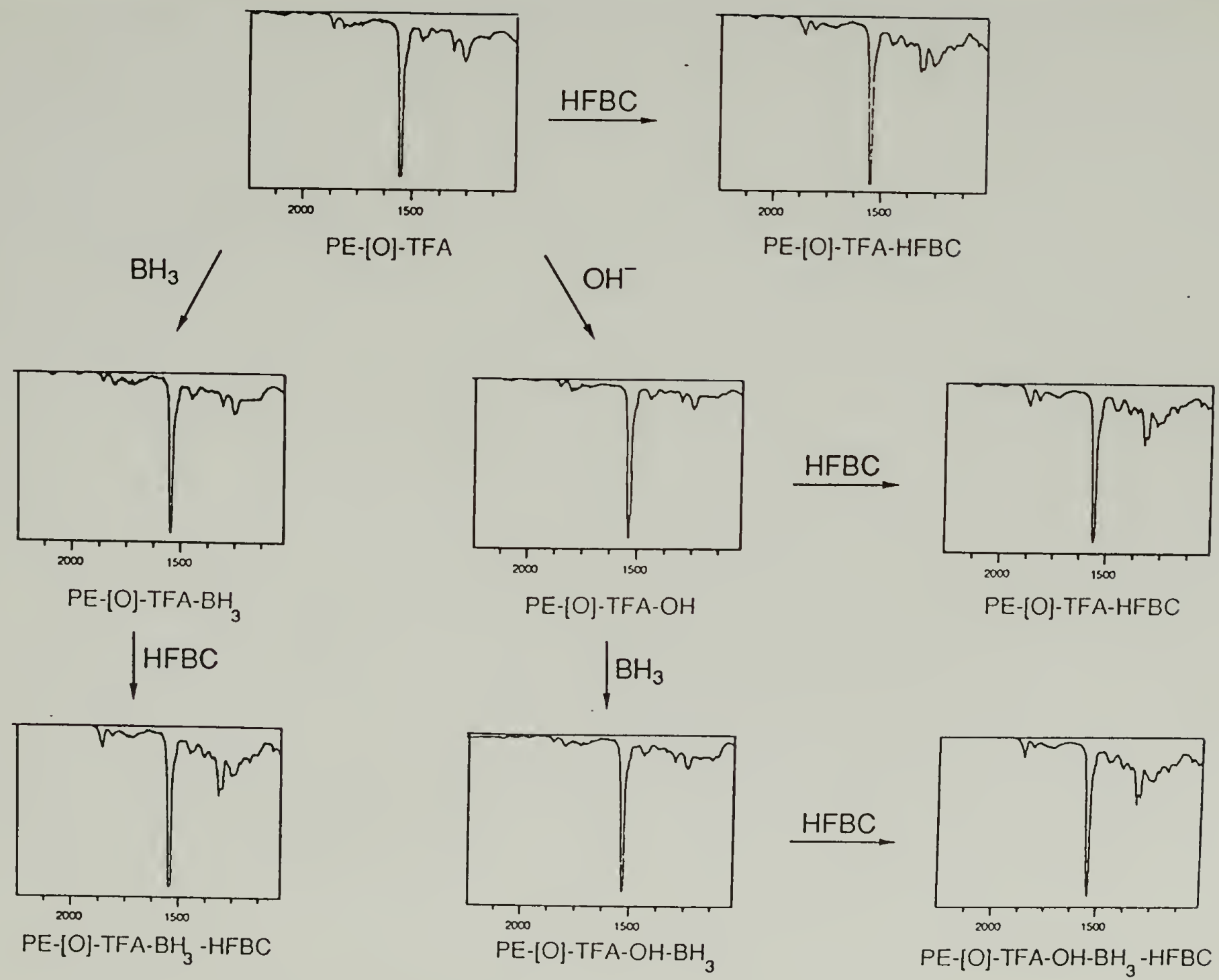


Figure 6.11. ATR-IR Spectra of Derivatized PE-[O]-TFA Surfaces.

carbons, and the PE-TFA-OH-BH_3 surface showed an uptake of 5. Based on the amount of oxygen on these surfaces not attached to TFA groups, we would have expected a greater percentage of fluorine in the XPS spectra after labeling. All indications are that the labeling reaction did not go as deep as the reaction depth, because we would have expected a significantly greater incorporation of fluorine for the depth of reaction indicated. The entire XPS sampling depth (10Å for grazing takeoff angle) may not have been accessible to labeling. These labeling experiments showed that all of the derivatization reactions resulted in nucleophilic surfaces which could be esterified to produce halogenated surfaces.

Contact angle data for the BH_3 reduction of this set of samples is also puzzling. One would expect that the contact angle of the hydrolyzed surface would either decrease or remain constant after reduction, but the receding angle increases to 50. We attribute this to reaction with HFBC as a contaminant, as discussed earlier. In previous reactions, BH_3 reduction and base hydrolysis of equivalent PE-TFA surfaces led to almost identical contact angles, which was reasonable when we considered that most of the TFA groups were also cleaved under the reduction conditions. Labeling with HFBC led to an increase in contact angle for all of the samples.

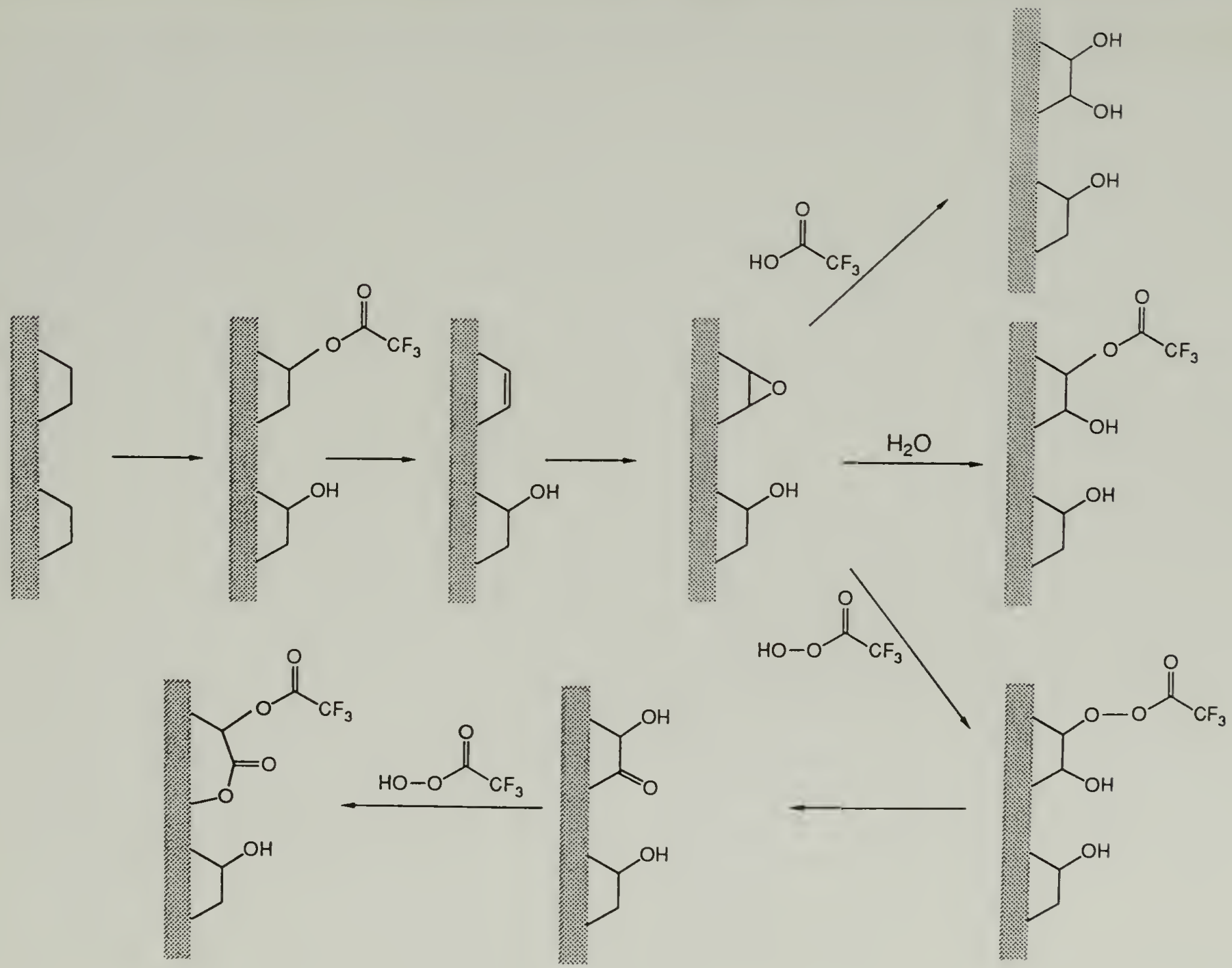
Conclusions

Essentially mild conditions created a mixture of hydroxyl and TFA groups on PE surfaces. This reaction proceeded deeply and rapidly because the modified layer was more more susceptible to oxidation than the nonfunctionalized portions of the PE chains. A combination of ATR-IR, XPS and contact angle data show us that the newly modified surface was made up of hydroxyl, trifluoroacetate, ketone and at least two types of ester groups. In the solution reaction, ketones are products only when tertiary carbon atoms are present. Our HDPE as received should contain a maximum of 6 branches per 1000 carbon atoms.[33] Even if each one had reacted with TFPAA to form a ketone, the concentration of

ketones would not be high enough to be seen within the ATR-IR sampling depth. The ketones and non-TFA esters groups must be formed by a different mechanism.

The reaction of PE with TFPAA should produce secondary alcohols as the initial products. We assume initially that the hydroxyl groups formed are spread far apart, based on the reports of TFPAA reaction with 1-decanol to form 1,10-decanediols, as opposed to other diols.[34-35] After prolonged reaction times, some of the solution products rearrange to form 2, 3 and 4 decanols in solution, so the density of functional groups at the surface could have increased. Some of the possible reaction pathways after the initial hydroxylation reaction are shown in Scheme 6.6. If we assume that the first products are isolated alcohols, these can be quickly esterified to TFA groups on the surfaces. These esters are reasonable leaving groups, and as predicted by the reactions observed in solution, we can expect elimination of the TFA groups, followed by epoxidation of the double bonds by TFPAA remaining in solution. These epoxides can be opened up in at least three ways, as shown in Scheme 6.6. As shown, the products can be diols, their TFA esters, or a diol/perester combination. The latter species can rearrange to form α-hydroxy ketones, and esters are then possible via Baeyer-Villiger reaction, as well as further oxidation products.[39]

The significant depth of our modified layer at very short reaction times led us to believe that these other reactions are occurring early in the reaction because they usually require less energy than the original hydroxylation. If the electronegative substituents were spread more evenly along the chains, they would discourage additional functionalization at nearby carbons, and the density of functional groups would not increase at an appreciable rate; the reaction becomes self limiting and we get further oxidation of the groups that have already been introduced.



Scheme 6.6. Product Mixtures formed from the TFPAA Oxidation of HDPE.

It is interesting to look at the "inhibitive" effect of hydroxyl groups in this situation, because the difference between intra- and intermolecular effects becomes blurred when a reaction takes place in the bulk. In solution reactions, the issue is more clear cut. There are usually solvent molecules separating the chains in a homogeneous reaction in solution. At a surface, it is difficult to know how far apart the chains are, even if the polymer/solvent interaction parameters are well defined. This would depend on the degree of swelling at the surface, and although PE should not be soluble in trifluoroacetic acid, the modified surface may be. The presence of polar groups on the same or neighboring chains may prevent further hydroxylation in this manner.

We used relatively harsh conditions to apply this reaction to PE and PP surfaces, hoping to increase the density of functional groups per chain. These conditions resulted in deeply modified surfaces and several types of functional group products. We found that reactions at a surface produced a different product distribution than we would expect based on the results of solution reactions. Reactions with *n*-alkanes in solution produced a mixture of secondary alcohols and trifluoroacetates, and no ketones or oxidation products of ketones. To avoid further oxidation, the solution studies have either used large excesses of alkane over TFPAA or they have stopped at a limited conversion of the starting material. This is difficult when the reaction takes place at a surface or within a polymer/solvent interface. For the reaction of TFPAA with PE, we have shown that longer reaction times and higher temperature broaden the distribution of products and do not necessarily increase the density of functional groups. Now that we know we can introduce these types of groups onto hydrocarbon polymers, we can tailor our reaction conditions to increase surface selectivity and narrow the distribution of products.

Clearly, an excess of reagents is a bigger problem for chemistry in two dimensions at polymer surfaces, but in our research group, we have shown repeatedly that the combination of temperature and solvent can be used to control the depth of reaction and the

sharpness of the interface between modified and virgin material. The interaction of a PE surface with TFPAA under very mild conditions should yield very interesting results. We might not achieve a very high density of functional groups, but a layer of ~7 TFA groups per 100 carbon atoms shows a significant increase in surface energy via contact angle changes from 108/75 to 99/42, and provides a mixture of alcohol and trifluoroacetate groups which can be treated as a protected hydroxyl surface. This array of functional groups could be further derivatized to form functional handles on the surface and the degree of esterification of the surface hydroxyl groups could be monitored by contact angle and XPS. Although the concentration of the newly introduced functional groups may be small, the impact of this type of surface modification capability on adhesion and interface problems may be quite large.

References

1. Dias, A. J.; McCarthy, T. J. *Macromolecules* **1984**, *17*, 2529.

2. Dias, A. J.; McCarthy, T. J. *Macromolecules* **1985**, *18*, 1826.

3. Dias, A. J.; McCarthy, T. J. *Macromolecules* **1987**, *20*, 2068.

4. Costello, C. A.; McCarthy, T. J. *Macromolecules* **1987**, *20*, 2819.

5. Costello, C. A.; McCarthy, T. J. *Macromolecules* **1984**, *17*, 2940.

6. Brennan, J. B.; McCarthy, T. J. *Polym. Preprints, ACS Div. Polym. Chem.* **1988**, *29(2)*, 336.

7. Bening, R. C.; McCarthy, T. J. *Polym. Preprints, ACS Div. Polym. Chem.* **1988**, *29(2)*, 338.

8. Ulrich, V. *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 701.

9. Augustine, R. L. Oxidation, Marcel Dekker, New York, 1969. Vols. 1 and 2.

10. Chinn, L. L. Selection of Oxidants in Synthesis, Oxidation at the Carbon Atom, Marcel Dekker, New York, 1971.

11. Ogawa, Y. I. *Tetrahedron Lett.* **1981**, 2277.

12. Zadok, E.; Mazur, Y. *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 303.

13. Walling, C. *Acc. Chem. Res.* **1975**, *8*, 125.

14. Chenier, J. H.; Tong, S. B.; Howard, J. A. *Can. J. Chem.* **1978**, *56*, 3047.

15. Williamson, D. G.; Cvetanovic, R. J. *J. Am. Chem. Soc.* **1970**, *92*, 2949.

16. Groves, J. T.; Nemo, T. E.; Myers, R. S. *J. Am. Chem. Soc.*, **1979**, *101*, 1032.

17. Mansuy, D.; Bartoli, J. F.; Chottard, J. C.; Lange, M. *Angew. Chem., Int Ed. Engl.* **1978**, *17*, 909.

18. Briggs, D. M.; Briggs, D. *Polymer* **1981**, *22*, 7.

19. Blais, P.; Carlsson, D. J.; Csullog, G.W.; Wiles, D.M. *J. Coll. Int. Sci.* **1974**, *47*, 636.

20. Rasmussen, J. R.; Stedronsky, E. R.; Whitesides, G.M. *J. Am. Chem. Soc.* **1977**, *99*, 4736.

21. Rasmussen, J. R.; Bergbreiter, D. E.; Whitesides, G.M. *J. Am. Chem. Soc.* **1977**, *99*, 4746.

22. Shilov, A. E. The Activation of Saturated hydrocarbons by Transition Metal Catalysts, D. Riedel Publishing Co.: Dordrecht, 1984.

23. Geletii,Y.V.; Zakharov, I.V.; Karasevich, E.I.; Shteinman, A. A. *Kinet. Katal.* **1981**, *22*, 349.

24. Geletii,Y.V.; Zakharov, I.V.; Karasevich, E.I.; Shteinman, A. A. *Kinet. Katal.* **1981**, *20*, 1124.

25. Karasevich, E.I.; Muradov, N.Z.; Shteinman, A. A. *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1974**, *8*, 1805.

26. Mimoun, H.; de Roch, I.S.; *Tetrahedron* **1975**, *31*, 777.

27. Lavrushko, V.V.; Khenkin, A.M.; Shilov, A.E. *Kinet. Katal.* **1980**, *21*, 276.

28. Dias, A. J. *Ph. D. Dissertation*, University of Massachusetts, Amherst, 1987.

29. Harrick, N. J. Internal Reflection Spectroscopy, Wiley Interscience: New York, **1981**.

30. Tsubokawa, N.; Fujiki, K.; Sone, Y. *J. Poly. Sci. Chem. Ed.* **1986**, *24*, 191.

31. Takaishi, N.; Fujikura, Y.; Inamoto, Y. *Synthesis* **1983**, 293.

32. Muller, W.; Schneider, H. J. *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 407.

33. Brandrup, J; Immergut, E.H. Polymer Handbook, Wiley Interscience, New York, 1975, IV-241.

34. Deno, N. H.; Jedziniak, J.; Messer, L.; Meyer, M.; Stroud, S.; Tomezco, E. *Tetrahedron* **1977**, *33*, 2503.

35. Deno, N. C.; Messer, L. A. *Chem. Comm.* **1976**, 1051.

36. Deno, N. C.; Gladfelter, E. J.; Pohl, D. G. *J. Org. Chem.* **1979**, *44*, 3728.

37. Cross, E. C.; McCarthy, T. J. *Macromolecules* **1987**, *23*, 3916.

38. Clark, D. T.; Thomas, H. R. *J. Appl. Polym. Sci. Polym. Chem. Ed.* **1977**, *15*, 2843.

39. Lowry, T. H.; Richardson, K. S. Mechanism and Theory in Organic Chemistry. Harper and Row, New York, 1987. Chapter 5.

APPENDIX

SYNTHESIS OF *SYN*-TRICYCLO[4.2.0.0^{2,5}]OCTA-3,7-DIENE

The stoichiometries used by Avram and Paquette are shown in Table 1 Both authors used similar procedures, except that Paquette advocated the use of HMPA as a co-solvent in the DCCB reduction. HMPA and DCCB were dried using CaH_2, except in V-31 where DCCB was dried with P_2O_5. Diethyl ether (Et_2O) was distilled from sodium and benzophenone. All DCCB was purchased from Fluka and was ≥ 98% purity, unless otherwise noted.

V-20 Preparation and Titration of Sodium Amalgam (0.5%)

A mixture of 500g of mercury and 2.5g of sodium spheres (Aldrich) were heated under nitrogen with a heating mantle in a 250ml 3N-RB flask to make 0.5% sodium amalgam. This was titrated by reacting a known amount of amalgam with a measured excess of 0.10N HCl. The acid/mercury solution was back-titrated with 0.10N NaOH to determine the amount of active sodium in a given quantity of amalgam. The effects of mechanical agitation vs. sonication for the titrations were investigated and shown to not be significant. Two of the samples were left out in the air for one hour before titrating to simulate the effects of using a graduate cylinder in the open air to measure the amount of sodium amalgam used in each reaction. The active sodium content measured in these samples agreed well with the samples titrated within 5 min, and the amalgam was measured out in the air in subsequent experiments without compensating for any loss of active sodium. Lithium amalgam was prepared in a similar manner, except that ribbons of fresh lithium metal were used in place of the sodium spheres.

Anti-TCOD (V-5,17,19)

Avram's procedure using lithium amalgam to make anti-TCOD was attempted both with and without the addition of HMPA as a cosolvent. In both cases, ^{1}H-NMR analysis indicated that the *syn* isomer was formed in equal or greater quantities with the anti isomer. Because a mixture of isomers was not optimal and because neither product was produced in appreciable yield, this procedure using lithium amalgam was abandoned in favor of the *syn*-TCOD prep with sodium amalgam. A procedure suggested by TMcC using butyl lithium as the reducing agent was also attempted (V-19), but initial NMR analysis of the reaction products did not look promising enough to continue.

Small Both Small and Large Scale Trials of *syn*-TCOD

syn TCOD was synthesized first on a small scale (V-9,19,23,25,27) and later on a larger one (V-31,55,59). The experimental description from reaction V-31 was used as the basis for this procedural summary. Modifications from the other larger scale reactions (V-55,59) are included as appropriate. Stoichiometries for the larger scale synthesis trials can be found in Appendix B.

A 1L-3N-RB flask was equipped with a 250ml addition funnel, a mechanical stirrer and a Liebig condenser. Glass beads (6mm, 2oz.) were added and the flask was purged with nitrogen. Sodium amalgam was measured into a 50 mL graduated cylinder and added to the reaction flask. After flushing the flask with nitrogen, the addition funnel was charged with 6.7 mL of DCCB, 42ml HMPA and 110ml Et_2O. A slight pink color resulted when the DCCB and HMPA were combined. This solution was added at a rate of 6mL/min to the stirred amalgam, forming a bi-layered reaction mixture of metallic colored amalgam and gray colored ether solution.

Reaction V-55 was noticeably exothermic, and the reaction flask for the next batch (V-59) was immersed in ice water during the addition. The ice was removed and the reaction was allowed to stir for 2 h. It was kept on ice overnight and then stirred for 12 h the next day. Total reaction time for V-59 was 14 h. The other two larger scale reactions (V-31,55) were stirred at room temperature for 10 and 31 h respectively. The reactions were sampled (0.5ml) periodically to determine the extent of reaction, using both GC and NMR. For each aliquot, the HMPA was washed out by shaking with 0.5 mL H_2O and a GC was run of the organic layer. The ether from this mixture was removed via trap to trap distillation at 0°C/35mm, and the resulting yellow oil was examined by NMR. Comparison of the ratio of DCCB to TCOD by GC and NMR gave inconsistent results, perhaps because the TCOD and DCCB distilled over with the Et_2O in different proportions each time in the trap to trap distillation. As a result of the inconsistencies in the data, reaction V-55 was run longer than might have been necessary, but this study did indicate that increased reaction time did not decrease the amount of *syn*-TCOD produced. No anti-TCOD resulted from the use of sodium amalgam as the reducing agent.

The reaction mixture was allowed to settle and the ether layer was filtered though a celite column (1.5"x12") which had been packed as a slurry. The amalgam layer was washed with ether (3x50 mL) and these portions were also filtered. After thoroughly flushing the column, the combined ether portions were distilled on the rotovap at ambient pressure to yield 50 mL of a viscous red/brown colored solution.

To remove the HMPA, extraction conditions were optimized using a sample of cyclooctene and HMPA present in similar quantities to the s-TCOD and HMPA in the reaction mixture. The best combination was a 1:1:1 mixture by volume of pentane, HMPA and the crude reaction products. For each of the reactions, the crude product was

diluted with 50 mL pentane (Et_2O in the case of V-31) and washed with 50 mL water. Analysis by GC showed that no HMPA was present in the ether layer. The aqueous layer was washed with pentane (4x50 mL) and the combined pentane portions distilled on the rotovap at ambient pressure to give 4.8g of a red-brown oil. The residual pentane was removed at 0°C/35mm. An ^{1}H-NMR of the oil indicated that DCCB and s-TCOD were present in a ratio of 1.3 to 1. Assuming that all of the starting material was present as either DCCB or s-TCOD, the reaction yield was 60%. Calculations for yield based on NMR integrations are found on page V-36.

Purification of s-TCOD via the silver complex of s-TCOD

Avram purified s-TCOD by forming a complex with silver, recrystallizing it from ethanol and regenerating s-TCOD by reaction with sodium chloride. To evaluate the efficiency of the Avram separation, one-sixth of the product mixture from V-31 (0.8g) was diluted with 12 mL Et_2O in a 50 mL erlenmeyer flask, 2 mL of a saturated $AgNO_3$ solution were added and the flask was shaken. A white precipitate formed immediately, but it turned yellow and then brown within 5 min. The ether/water layer was removed with a pipet and the brown solid was washed with 3 small portion of ether to remove any soluble impurities. Without drying the solid, 4 mL of saturated NaCl solution which had been chilled to -5°C were added to the flask and it was shaken vigorously by hand for 10 min. The complex immediately turned a metallic gray color and coated the sides of the flask completely. At approximately 9 min, the consistency of the solution changed abruptly and it would not wet the sides of the flask. It was most helpful to listen to Blondie during this part of the procedure. The liquid phase was transferred to a small testube, and a yellow layer of oil collected both at the top of the testube and on the surface of the gray solid remaining in the flask. ^{1}H-NMR of this oil showed s-TCOD mixed with Et_2O, and only traces of DCCB. There was also a peak at 4.4ppm which could have been due to a HNO_3 moiety, but this disappeared after extracting the NMR sample with water.

Larger Scale Purification of s-TCOD via the Silver complex:

The remaining product solution from V-31 was shaken with 10 mL of saturated $AgNO_3$ to give the same brown solid as observed on the small scale. After washing with 3x5 mL portions of ether, the complex was dried under vacuum overnight at 50mTorr. The soft brown solid was crushed using a mortar and pestel and divided into 2 erlenmeyer flasks (one and two thirds by weight, respectively.) Avram used ethanol as a recrystallization solvent, but small scale attempts demonstrated that a large proportion of the brown solid was not soluble. Cooling the more concentrated sample yielded a white precipitate which indicated that some of the Ag^+ complex of s-TCOD was present. The 5g batch was extracted with hot ethanol (6x5 mL) and the resulting yellow solution was removed via rotovap at reduced pressure to give a yellow crystalline solid. Some of this material melted at 136-140°C (lit. mp 138-140°C), but some of the solid turned brown and had not melted at 154°C. The yield from this larger scale recrystallization was not encouraging, and was not consistent with the 60% indicated by NMR of the crude product. An impurity formed by reaction of DCCB with the $AgNO_3$ may have interfered with the separation procedure, but in any case, a more practical means of purification was needed for batches V-55, 59.

Purification of of s-TCOD by Spinning Band Distillation

In order to optimize the total yield of TCOD, the product mixtures from 5.55 and 5.59 were diluted with chlorobenzene and heptane and then distilled on a spinning band column (V-65) to separate TCOD from DCCB and any other impurities present. The low boiling impurities distill over before the heptane, and the chlorobenzene should stop the higher boiling impurities from coming over with the TCOD. These diluents were chosen (see Table 2) specifically for their applicability to the olefin metathesis reactions. Heptane

was suitable as an internal standard for TCOD given the GC columns available, and chlorobenzene was a common solvent for these reactions.

The combined products of 5.55 and 59 were diluted with heptane and chlorobenzene. Before opening the system to vacuum (40 mm), the pot was cooled with an ethanol/liquid nitrogen bath to -40°C. There was no response from the solenoid, i.e. no volatile products, until the pot was at 20°C. The effect of the mass of chlorobenzene on the temperature required to volatilize the heptane and TCOD was not taken into account when setting the pressure, and the pot did not boil even at 50°C, although some heptane and other low boiling materials were collected. Because thermal decomposition was a potential problem, the pot was cooled and the vacuum lowered to 30mm. TCOD collection began at a head temperature of 51-53°C and fractions E through N were collected quickly to avoid excessive heating.

An Analabs Superpak II column (70°C) was used to analyze fractions from the spinning band distillation of TCOD. GC analysis of the fractions from the spinning band distillation showed that s-TCOD was synthesized in 30% yield to give 3.1g of a colorless oil which was mixed with heptane and chlorobenzene in varying proportions.

BIBLIOGRAPHY

Alimuniar, A. B.; Edwards, J. H.; Feast, W. J. "Metathesis Ring-Opening Polymerisation of Some Chlorinated Bicyclic Dienes" *J. Mol. Catal.* **1985**, *28*, 313.

Amass, A. J.; McGourtey, T. A.; Tuck, C. N. "Tungsten Hexachloride Alone as a Catalyst for the Metathetic Polymerization of Cyclic Olefins" *Eur. Polym. J.* **1976**, *12*, 93.

Ast, W.; Rheinwald, G.; Kerber, R. "Olefin Metathesis of Unsaturated Ethers" *Rec. Trav. Chim. Pays-Bas* **1977**, *96*, M127.

Augustine, R. L. Oxidation, Marcel Dekker, New York, 1969. Vols. 1 and 2.

Banasiak, D. S. "Insect Pheromones From Olefin Metathesis" *J. Mol. Catal.* **1985**, *28*, 107.

Boelhouwer, C. "Functionalized Olefin Metathesis" *J. Mol. Catal.* **1988**, *46*, 297.

Brandrup, J; Immergut, E.H. Polymer Handbook. Wiley Interscience, New York, 1975.

Brunthaler, J. K.; Stelzer, F.; Leising, G. "Ring-Opening Metathesis of *cis*-3,4-Dichlorocyclobutene and 3,4-Diisopropylcyclobutene: Evidence of a Polymer with Conjugated Double Bonds" *J. Mol. Catal.* **1985**, *28*, 393.

Canjii, E.; Perner, H. "Structure Determination of Polybutadiene and Butadiene-styrene Copolymers by Means of Metathesis Reaction" *Rec. Trav. Chim. Pays-Bas* **1977**, *96*, M70.

Castner, K. F.; Calderon, N. "Ring-Opening Polymerization of Cyclic Olefins Substituted with Polar Groups" *J. Mol. Catal.* **1982**, *15*, 47.

Chien, J. C.W. Polyacetylene, Academic, Orlando Fla, 1984.

Chinn, L. L. Selection of Oxidants in Synthesis, Oxidation at the Carbon Atom, Marcel Dekker, New York, 1971.

Coleman, C.G.; McCarthy, T.J. "Tricyclooctadiene: A Crosslinking Agent for Olefin Metathesis Polymerization:" *Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem.* **1988**, 29(1), 283.

Dall'Asta, G.; Manetti, R. "Synthesis and Properties of Crystalline trans-Polydecenamer" *Eur. Polym. J.* **1968**, *4*, 145.

Deno, N. C.; Gladfelter, E. J.; Pohl, D. G. "Selective Formation of 2-Chloroalkanes from Linear Alkanes" *J. Org. Chem.* **1979**, *44*, 3728.

Deno, N. C.; Messer, L. A. "Hydroxylation of Cyclohexane, Octan-1-ol, and Palmitic Acid by Trifluoroperoxyacetic Acid" *Chem. Comm.* **1976**, 1051.

Doyle, G. "Olefin Metathesis Catalyzed by Zero-Valent, Anionic Group VI Metal Compounds" *J. Catal.* **1973**, *30*, 118.

Draguton, V.; Balabon, A. T.; Dinonie, M.; Olefin Metathesis and Ring-Opening Polymerization of Cyclo-Olefins, Wiley-Interscience, Chinchester, 1985.

Edwards, J. H.; Feast, W. J.; Bott, D. C. "New Routes to Conjugated Polymers: 1. A Two Step Route to Polyacetylene" *Polymer* **1984**, *25*, 395.

El Saafin, I. F.; Feast, J. W. "Metathesis Polymerization of Arylpolycyclic Olefins" *J. Mol. Catal.* **1982**, *15*, 61.

Ellison, A.; Coverdale, A. K.; Dearing, P. F. "The Metathesis of Unsaturated Esters Over Re_2O_7/Al_2O_3" *J. Mol. Catal.* **1985**, *28*, 141.

Flory, P.J. Principles of Polymer Chemistry, Cornell Univ. Press, Ithaca, 1953.

Grubbs, R. H.; Tumas, W. "Polymer Synthesis and Organotransition Metal Chemistry" *Science* **1989**, *243*, 907.

Grubbs, R.H., in Compendium of Organometallic Chemistry, Wilkenson, G.; Stone, F. G. A.; Asbel, E. W. Eds.; Pergamon Press, Ltd.; Oxford, **1982**; Vol. 8, p. 499.

Harrick, N. J. Internal Reflection Spectroscopy, Wiley Interscience: New York, **1981**.

Ho, H.T.; Ivin, K. J.; Rooney, R. R. "Tactiticy and Stereochemistry in the Ring-Opening Polymerization of 5,5-Dimethylbicyclo[2.2.1] Hept-2-ene Initiated by Metathesis Catalysts" *J. Mol. Catal.* **1982**, *15*, 245.

Hocks, L.; Berck, D.; Hubert, A. J.; Teyssie, P. "Metathesis Catalysts III: Disproportionation of *cis*, *trans* -Cyclodeca-1,5-Diene and the Thermodynamic Stability of Cyclohexene" *J. Polym. Sci., Polym. Lett. Ed.* **1975**, *13*, 391.

Holtrup, W.; Streck, R.; Zaar, W.; Zerpner, D. "Preparation and Polymerization of 1,4-Cyclooctadiene" *J. Mol. Catal.* **1986**, *36*, 127.

Hummel, K. "Application of Olefin Metathesis to the Investigation of Polymer Structures" *J. Mol. Catal.* **1985**, *28*, 381.

Hummel, K.; Lechner, H.; Pongratz, T. "Investigation of Crosslinks in Polymers by Metathesis Reaction: Dehydrodimers of 1,5,9-Cyclododecatriene as Model Compounds" *J. Mol. Catal.* **1986**, *36*, 177.

Hummel, K.; Lechner, H.; Zekoll, H.; Chemelli, R. "Metathesis Degradation of Poly(butadiene-*alt*-propene)" *Makromol. Chem.* **1987**, *188*, 1075.

Ivin, K. J. Olefin Metathesis, Academic Press, London, 1983.

Ivin, K. J.; Saegusa, T. Ring-Opening Polymerization, Elsevier, London 1984. Vol. I.

Korshak, Y. V.; Dolgoplosk, B. A.; Tlenkopachev, M. A. "Cyclodegradation of Polyalkenamers in Solutions Acted on by Disproportionation Catalysts" *Rec. Trav. Chim. Pays-Bas* **1977**, *96*, M64.

Korshak, Y. V.; Tlenkopatchev, M.A.; Dolgoplosk, B. A.; Avdeikina, E. G.; Kutepov, D. F. "Intra- and Intermolecular Metathesis Reactions in the Formation and Degradation of Unsaturated Polymers" *J. Mol. Catal.* **1982**, *15*, 207.

Lowry, T. H.; Richardson, K. S. Mechanism and Theory in Organic Chemistry. Harper and Row, New York, 1987. Chapter 5.

March, J. Advanced Organic Chemistry, Wiley-Interscience, New York, 1985, 3rd ed. p. 914, 924.

Matejka, L.; Houtman, C.; Macosko, C. W. "Polymerization of Dicyclopentadiene: A New Reaction Injection Molding System" *J. Appl Polym. Sci.* **1985**, *30*, 2787.

Mol, J. C. "Metathesis of Functionalized Olefins" *J. Mol. Catal.* **1982**, *15*, 35.

Mol, J. C. Moulijn,J. A. "The Metathesis of Unsaturated Hydrocarbons Catalyzed by Transition Metal Compounds" *Adv Catal.* **1975**, *24*, 131.

Odian, G. Principles of Polymerization, Wiley-Interscience, New York, 1985. 2nd Ed, p. 268.

Sheldon, R. A.; Kochi, J. K. Metal-Catalyzed Oxidations of Organic Compounds. Academic Press, New York, 1981.

Shilov, A. E. The Activation of Saturated hydrocarbons by Transition Metal Catalysts. D. Riedel Publishing Co., Dordrecht, 1984.

Shriver, D. F. Manipulations of Air Sensitive Compounds. McGraw-Hill, New York, 1969.

Stelzer, F.; Hobisch, G.; Pongratz, T.; Hummel, K. "Metathesis Degradation of Acrylonitrile/Butadiene Copolymers" *J. Mol. Catal.* **1988**, *46*, 433.

Streck, R. "Olefin Metathesis in Industry: A Status Report" *J. Mol. Catal.* **1988**, *46*, 305.

Streck, R. "Some Applications of the Olefin Metathesis Reaction to Polymer Synthesis" *J. Mol. Catal.* **1982**, *15*, 3.

Thoi, H. H.; Reddy, B. S. R.; Rooney, J. J. "Some Aspects of Stereoselectivities and Kinetics in the Ring-opening Polymerization of Norbornenes using Metathesis Catalysts" *J. Chem Soc., Faraday Trans. I* **1982**, *78*, 3307.

Thorn-Csanyi, E.; Perner, H. "Quantitative Microstructure Determination of Diene Polymers by Means of Metathesis Degradation" *J. Mol. Catal.***1986**, *36*, 187.

Treloar, L. R. G. The Physics of Rubber Elasticity. Oxford, London, 1958.

Verkuijlen, E.; Boelhouwer, C. "Formation of Cyclohexa-1,4-diene by Metathesis of Linoleic and Linolenic esters" *Chem. Commun.* **1974**, 793.

Verluijlen, E.; Dirks, R. J.; Boelhouwer, C. "Metathesis of Low-Molecular Unsaturated Acid Esters" *Rec. Trav. Chim. Pays-Bas* **1977**, *96*, M86.

Zang, Y. H.; Muller, R.; Froelich, D. "Determination of Crosslinking Density of Polymer Networks by Mechanical Data in Simple Extension and by Swelling Degree at Equilibrium" *Polymer* **1989**, *30*, 2060.